CHEMICAL ABSTRACTS

Vol. 15. OCTOBER 20, 1921 No. 20

1—APPARATUS

C. G. DERICK

A comparison of British and German volumetric glassware. J. E. PETAVEL. Natl. Phys. Lab. *Nature* **107**, 297–8(1921).—Tabulated results of tests made with Brit. and Ger. pipets and flasks of different capacities show that the ordinary grade of Ger. app. has no claim to superior accuracy as compared with the ordinary grade of Brit. app. W. H. ROSS

Cleaning and keeping clean volumetric apparatus. RAGNAR BERG. *Chem. Ztg.* **45**, 749(1921).—The oil film on burets, etc., may also be due to oil from the rubber used with pinchcock clamps and to hydrocarbons resulting from burning illuminating gas. Cf. Horst, *C. A.* **15**, 3229. J. H. MOORE

An apparatus for industrial gas analysis. G. ANDOYER. *Compt. rend.* **173**, 237–8 (1921).—The app. is designed to correct some of the faults and combine the merits of the Hemple and Orsat forms. It consists of a graduated cylindrical tube surrounded by a water mantle and drawn out to a narrow tube at both ends. The lower end is connected by rubber tubing with a leveling bottle and the upper end leads to a 3-way stopcock which is the 0 point of the calibration. Through the stopcock the gas is introduced and removed; the third opening leads to a funnel through which water is added to rinse absorbents out of the boring. With the app. 2 lab. pipets of the Orsat type are supplied as well as an explosion pipet and one for combustion by means of glowing Pt or Pd. W. T. HALL

A device for titrating. VLADO PRELOG. Osijek. *Chem. Ztg.* **45**, 736(1921).—The buret holder is clamped to the neck of the stock bottle and the buret is filled by sucking through a tube connected to a T in the top of the buret, the other arm of the T being connected to a tube leading to the bottom of the stock bottle. J. H. MOORE

Extraction apparatus and extraction practice. H. Voss. Fockbek. *Chem. Ztg.* **45**, 721–3, 743–6(1921).—(I) The 1st part of the article discusses "Properties of solvents," "Extns. in general," "Detn. of the size of app.," "Detn. of the size of the solvent evaporator," "Detn. of the area of the heating surface in evaporators," "Detn. of the size of the condenser," "Detn. of the size of the solvent container," "Steam consumption," "Pipes for the solvent vapors," "Pipes for the liquids," with formulas for obtaining these. (II) The 2nd part is "Description and operation of extn. app. of different systems," under the headings: "The single effect," "Multiple effect extractors," "Extractors for bulky materials," "Cadaver extn. app.," "Ceresin residues," "Stearin residues and wool grease slime," "Raw wool," "Castor oil press-cake," "Beeswax residues," "Gutta-percha and caoutchouc," "Gas-purification materials," and "Fish." J. H. MOORE

A new densimeter for gases. HENRY HAUSER. *Anales soc. espaň. fis. quim.* **18**, 79–82(1920).—Within a tall glass bell is placed a cylinder of water (or oil) in which floats a hydrometer with a slender stem, the protruding end of which is expanded into a large thin-walled bulb. The gas to be tested passes through the bell in a slow stream. Variations in the density of the gas cause the hydrometer to float higher or lower and the density is read from a scale engraved on the stem. L. E. GILSON

A new fusel oil tester. A. NOLL. Tilsit. *Chem. Ztg.* **45**, 678(1921).—The app. is a long-neck flask, with ground stopper, holding 30 cc. up to a mark near the bottom of the neck. Above this mark there are 2 scales, 1 graduated upward from 30–40 cc. and the other downward from 0 (the 40-cc. mark on the 1st scale) to 10 cc., the graduation being in 0.1 cc. To operate, the app. is filled to the 30-cc. mark with a $CaCl_2$ soln. of 1.225 sp. gr., 10 cc. of the fusel oil carefully run in on top of the soln., the stopper inserted, the app. shaken well and carefully, the oil allowed to sep. and the volume read on the scale. The decrease in vol. represents the H_2O in the oil. J. H. MOORE

Acid pumps without stuffing boxes. HANS FINKELSTEIN. *Chem. Ztg.* **45**, 698–9 (1921).—Comments on an article by Rabe (*C. A.* **15**, 1953) on centrifugal pumps and the flow of liquids. The Larass turbine pump without stuffing boxes is described and illustrated. C. C. DAVIS

Check valve. W. NORMANN. *Chem. Ztg.* **45**, 712(1921).—The valve is described in Lassar-Cohn's "Arbeitsmethoden," vol. I, p. 63. It consists of a long tube of small bore connected to the app. to be exhausted, the lower end dipping under Hg in a small bottle with a 2-hole stopper, the other hole being connected to the H_2O pump. Cf. *C. A.* **15**, 3, 2368. J. H. MOORE

Electric oven for baking pencil leads. GORDON WEAVER. *Elec. World* **78**, 514 (1921); 2 illus.—Details of operation and costs are given. C. G. F.

Crucibles (U. S. pat. 1,381,171) **19.**

Photochemical apparatus. W. O. SNELLING. U. S. 1,382,252, June 21. The app. is adapted for halogenating hydrocarbons. It comprizes a transparent dome inverted over a liquid-filled pan through which pass inlet and outlet pipes. A lamp supplying actinic rays is placed adjacent the dome.

Apparatus for extracting oils, fats, grease, rubber, sulfur or other materials with solvents. L. J. SIMON and J. W. HINCHLEY. U. S. 1,381,758, June 14.

Apparatus for electrically heating and sterilizing water or other liquids. L. G. ABOGADO. U. S. 1,382,156–7–8–9, June 21. An elec. current is passed through a moving film of the liquid.

Apparatus for bleaching almonds. G. W. PIERCE. U. S. 1,382,850, June 28. The almonds are carried in a rotary agitator while exposed to the action of SO_2.

2—GENERAL AND PHYSICAL CHEMISTRY

W. E. HENDERSON AND EDWARD MACK

Robert Andrews Millikan. ANON. *Elec. World* **78**, 502(1921).—A biographical sketch. C. G. F.

Theodor Diehl. HANS ALEXANDER. *Z. angew. Chem.* **34**, Aufsatzteil, 421–2 (1921).—An obituary. E. J. C.

Celso Ulpiani. ANON. *Staz. sper. agrar. ital.* **52**, 603–4(1919).—An obituary. ALBERT R. MERZ

The Bureau of Mines and private investigations. H. FOSTER BAIN. *Eng. Mining J.* **112**, 450–3(1921).—The nature of the "contacts" is discussed. E. J. C.

Science in the service of the state. T. G. TREVOR. *S. African J. Ind.* **4**, 608–12(1921). E. J. C.

List of French laboratories. CH. MAURAIN. *Bull. officiel direction recherches sci. ind. inventions* 1921, 372–84, 437–48. E. J. C.

Molecular structure and energy. ALAN W. C. MENZIES. Princeton Univ. *Nature* **107**, 331(1921).—The structures of CO_2, N_2O and N mols. are discussed with a view

to meeting the difficulties in the Lewis-Langmuir theory as pointed out by Partington (*C. A.* **15**, 2237). W. H. Ross

Optical refraction at corresponding temperatures. W. Herz. Univ. Breslau. *Z. physik. Chem.* **98**, 175–80(1921).—Available data show that within certain limits the index of refraction of all substances at the crit. temp. has the value 1.126. Accordingly the Lorenz-Lorentz and Gladstone-Dale formulas give approx. the same values for the refractivity at the crit. temp. Also at other corresponding temps. the index of refraction of different substances has approx. const. values, although the differences may be greater than at the crit. temp. H. Jermain Creighton

The resistivity of selenium. H. Pélabon. *Compt. rend.* **173**, 295–7(1921).—Measurements on liquid Se, using Au electrodes, were made from 390° to 690°. The resistivity is given by $\log \rho = 8.506 - 0.0095t$. Approaching 300° the resistance of Se diminishes suddenly, reaching a min. at about 300°. It then rises to a max. below 260° and again diminishes. At lower temps. the resistance depends on the treatment and is not simply a function of the temp. At room temp. the variations are greater than the min. value of the resistance. E. D. Williamson

The nature of the electrical conductivity of glass. Horace H. Poole. *Nature* **107**, 584–5(1921).—Exptl. evidence is given in support of the view that the elec. cond. of glass is largely, if not entirely, of a nonelectrolytic nature. W. H. Ross

Acidity and basicity. Rudolf Keller. Prague. *Z. physik. Chem.* **98**, 338–51 (1921).—A theoretical paper. It is pointed out that for ascertaining the acidity of the combination solute-solvent, not merely must the internal chem. constitution of the former be taken into consideration, but also the chem. constitution of the solvent. This is especially important with amphoteric solutes. Further, the difference between the dielec. const. of the solute and solvent must be considered. This, too, is most marked in the case of amphoteric, undissociated and associated solutes. The so-called basic dyes which usually migrate towards the anode are, therefore, according to prevailing nomenclature, acid, especially the course-dispersed, undissociated dyes. On the other hand, the so-called acid dyes are mostly basic or amphoteric. Certain acid dyes, *e. g.*, $C_6H_2(NO_2)_3OH$, Martius' yellow, aurantia, are really acid and migrate towards the anode. It is pointed out that while the *Fichter-Sahlbom capillary rule* is described correctly, it is incorrectly defined, as, without exception, all capillary expts. show that on dipping strips of paper into solns. of dyes, negative substances are distributed evenly on the paper, while neutral and positive substances are deposited only on the upper portion of the paper. The direction of migration of strong acids and bases (HCl, H_2SO_4, KOH) in certain dispersion media is opposite to that which corresponds to their nature. It is possible to construct concn. chains in which the strongest acids behave as bases and *vice versa*.

H. Jermain Creighton

The action of neutral salts at high salt concentrations on the velocity of saponification of ethyl acetate and on the activity of the hydrogen ion of the catalyst. Gösta Åkerlöf. Nobelinst., Stockholm. *Z. physik. Chem.* **98**, 260–92(1921); *Medd. Vetenskapsakad. Nobelinst.* **4**, No. 13, 40 pp.(1921).—Velocity measurements at const. titer-acidity have been made in conjunction with measurements of the H-ion activity, in order to find the cause of the action of neutral salts on reaction velocity The measurements were carried out at 25°, and HCl, HNO_3 and H_2SO_4 were employed as catalysts. It has been found that the relation between the velocity of sapon. (K) and the H-ion activity (α) is expressed by the equation, $K = C_\alpha . f(n) . \sqrt[3]{\alpha}$, where n is the concn. of the catalyst (titer-acidity) and the other quantities are consts. As far as has been detd. this formula holds for all concns. of catalyst, and is independent of the nature of the catalyst or the salt present. The expression is not only valid for sapon., but also holds for the inversion of sugar and other related reactions. In view of the results, it would

appear that the *current theory of the catalytic activity* of the undissociated mol. is not correct. The salt mol. does not possess any activity of its own, but is merely the cause of the change in the activity of the catalyst. It is not known, however, in what manner this change is brought about by the neutral salt, but the most probable hypothesis is that it effects a change in the H_2O envelopes surrounding the H ions. The concn. of the H ions remains const. while their activity undergoes a change. According to this hypothesis the hydration numbers are not definite quantities; but the ions exert a control on all H_2O mols. present in soln. H. JERMAIN CREIGHTON

Theory of catalysis in homogeneous gas reactions. KARL F. HERZFELD. Munich. *Z. physik. Chem.* **98**, 161-74(1921).—The problem treated is why a reaction by way of intermediate products proceeds more rapidly than when it follows the direct path. Since, at all concns., the velocity of the complete reaction is detd. by that of the slowest partial reaction, it follows that this partial reaction must be more rapid than the direct reaction, if catalysis takes place. It is shown that if catalysis is to take place (the concn. of the catalyst being not too small) then it is necessary that the heat of activation of the intermediate product (in reality its heat of formation from its ats.) is essentially smaller than that of the starting product. In the most favorable case the heat of activation of the former is approx. one-half that of the latter. There exists, therefore, an upper limit for the acceleration that may be attained with an individual catalyst at a not too high concn. H. JERMAIN CREIGHTON

A general theory of electrolytic solutions. JNANEND CHANDRA GHOSH. Univ. Calcutta. *Z. physik. Chem.* **98**, 211-38(1921).—The following equation is derived for the work (A) that is necessary to sep. completely a g. mol. of ions from one another: $A=3N.E^2.2\sqrt[3]{2N}/D\sqrt[3]{3}\sqrt[3]{V}$, where N is the number of doublets present, E is the abs. elec. charge (4.7×10^{-10} e.s.u.), D is the dielec. const. of the solvent and V the cc. of soln. contg. a g. mol. The expressions $(NE^2\sqrt[3]{2N}/2RT.D)\{(1/\sqrt[3]{V_1})-(1/\sqrt[3]{V_2})\}=\ln(\mu_{V_2}/\mu_{V_1})$ and $(6NE^2\sqrt[3]{2N}/3RT.\sqrt[3]{3}D)\{(1\sqrt[3]{/V_1})-(1/\sqrt[3]{V_2})\}=\ln(\mu_{V_2}/\mu_{V_1})$, which contain only the natural consts. N, E and R have been developed for the mol. cond. of electrolytes of the type MA and MA_2, resp. These equations have been used to calc. the mol. cond. of KCl, NaCl, LiCl, CsCl, NH_4Cl, KBr, KI, $NaNO_3$, CH_3CO_2K, $BaCl_2$, $SrCl_2$ and $CaCl_2$ at dilns. of 10, 20, 1000 and 5000 l. The values obtained agree closely with those obtained by exptl. measurement. Equally good results have been obtained with these equations for the mol. cond. of NaI, NaBr, KI, SrI_2 and HCl in MeOH, and of KI in EtOH, as well as for the mol. cond. of $N(C_2H_5)_4I$ in 12 org. solvents. The equations, however, do not express correctly the change in the mol. cond. with diln., in the case of aq. solns. of strong acids and bases, although the irregularity disappears in non-aq. solns. of strong acids. For medium and strong electrolytes the diln. formula $(\alpha x)^2/(1-x)V=K$ gives const. values for K over a large range of concns. On the basis of Clausius' virial theorem it is shown that the relation between the osmotic pressure of salt solns. and the degree of dissociation of the salt is given by the expression $PV=nRT+(nRT\log\alpha)/3$. From this it follows that the abnormality factor $i=n(1+\ln\alpha/3)$. Values calcd. by means of this expression agree with exptl. results. In addition to the foregoing, the following topics are treated briefly: the influence of salts on the soly. of other salts, and the absorption of light by salt solns. H. JERMAIN CREIGHTON

Influence of some compounds on the viscosity of solutions of dextrose in water. SVETOZARA VARIĆAK. *Rev. chim.* **1**, 57-71(1921).—V. records a set of measurements of the coeff. of viscosity, at temps. between 5° and 40°, of solns. in water of HCl, KOH, tartaric acid, acetamide, and dextrose, and for mixts. of solns. of dextrose with solns. of each of the other four substances, the concns. ranging from 1 to 0.1 g. mol. of each solute per l. In all cases the general tendency is for the viscosity to decrease with rising temp., but, in the neighborhood of 25°, there is usually a fairly abrupt change in

the direction of the viscosity-temp. curve. Thus the viscosities of mixts. of solns. of acetamide and dextrose decrease rapidly with rising temp. from 5° to 25°, but remain nearly const. from 25° to 40°. In most other instances, the fall of viscosity from 5° to 25° is relatively slight, but a rapid fall takes place between 25° and 40°, the viscosities at this temp. for corresponding concns. being in all cases of about the same magnitude. J. C. S.

The relation between heat of solution and heat of fusion of organic substances. GEORG GEHLHOFF. Berlin-Friedenau. *Z. physik. Chem.* **98,** 252–9(1921).—Calorimetric detns. have been made of the heat of soln. of 18 org. compds. in 10 different solvents. The results obtained show that for hydrocarbons, aromatic amines, urethan and azobenzene, the heat of soln. is practically independent of the solvent and is approx. equal to the heat of fusion. For substances containing OH the heat of soln. varies very considerably with the nature of the solvent. Substances contg. NO_2 are intermediate between these 2 groups of compds. Detns. have also been made of the heat of soln. of NH_4, K and Na halides in H_2O. The values obtained are discussed with respect to the ion lattice structure of these salts. H. JERMAIN CREIGHTON

Progress report on symbols in heat engineering. W. D. ENNIS, *et al. Mech. Eng.* **43,** 623(1921).—Rept. of a committee of the Am. Soc. Mech. Eng. E. J. C.

Solubility of water in gasoline and in certain other organic liquids determined by the calcium chloride method. CHARLES W. CLIFFORD. *J. Ind. Eng. Chem.* **13,** 631–2 (1921).—The solvents are gasoline, benzene, $CHCl_3$, CCl_4 and CS_2. An increase in soly. accompanies an increase in temp. in each case. D. K. FRENCH

Ice crystals which form on bare soils and on the stems of plants. VICTOR BIRCKNER. *J. Wash. Acad. Sci.* **11,** 221–2(1921).—Ice crystals collected from bare soils, and especially from stems of *Cunila origanoides*, contain small amts. of org. matter which seems to be an unsatd. aromatic compd. probably of the styrolene group. The melted crystals support the growth of a bacterium identical with one which is able to use coumarin as a source of C. T. G. PHILLIPS

Report of special committee on the Baumé scale. W. D. HORNE, *et al. J. Assoc. Official Agr. Chem.* **4,** 551(1921).—It is recommended that the Baumé scale of the Bur. of Standards (Modulus 145), Table 31 (*C. A.* **13,** 384) be adopted as the official Baumé scale of the A. O. A. C., and that all Baumé tables and references thereto which are not in accordance with this scale be eliminated from the methods of the association. E. J. C.

The arc spectrum of terbium (a new element called welsium)(EDER) **3.** Signaling by invisible rays (BELL, MARSHALL) **3.**

PLANCK, MAX: **Vorlesunge über Thermodynamik.** Berlin and Leipzig: Verleger Walter de Gruyter and Co. 292 pp. M 45.

3—SUBATOMIC PHENOMENA AND RADIOCHEMISTRY

GERALD L. WENDT

Historical development of the atomic theory. GEORG LOCKEMANN. *Umschau* **25,** 181–6(1921).—This paper is an historical sketch of the ideas regarding atoms from Thales in 600 B. C. to the present time. No exptl. work or new theory is given. F. E. BROWN

The significance of new discoveries in the region of rays of very high frequency. MAURICE DE BROGLIE. *Scientia* **27,** 102–11(1920).—The theories of X-rays, and visible light rays, and their effects on different regions of electrons in the atom as well as the

diffraction of X-rays, radio-activity, and quantum theory are discussed briefly, and the belief is expressed that the wave theory of light should be carefully reëxamd. The field of very high wave frequency offers a large and fruitful field for investigation and development of new mechanical principles. The study of these short waves in relation to at. structure is of increasing importance. F. E. BROWN

Quaternian series and isotopes. F. H. LORING. *Chem. News* **123**, 38(1921).—A similarity of the arrangement of the series A, Fe, Br, and Ag is shown when the lower mass isotopes are compared with the higher mass isotopes and the old at. wts. [Two misprints occur: Fe = 59.9 should be Fe = 55.9; 11–40 should be 111–40. ABSTRACTOR.] L. D. ROBERTS

Note on my communication: A spectroscopic confirmation of the isotopy of chlorine. A. KRATZER. *Z. Physik* **4**, 476(1921).—K. points out that Loomis (*C. A.* **15**, 1254) has come to the same conclusion as he has (*C. A.* **15**, 1452). F. C. HOYT

Relationships between the constants of radioactive elements. HANS TH. WOLFF. Dresden. *Physik. Z.* **22**, 171–3(1921); cf. *C. A.* **14**, 3356.—W.'s previous formula, $\log R = x \log (k-s)+y$, can be expressed $\log R = \xi \log (0.75\ M-L+K)+\eta$ where M = at. wt., L = at. no., and ξ, K and η are consts. This formula applies to all α radiators except Th C, Ra F, Act X, Act C and Act C′, provided a special set of values is given the consts. for the members of the series U_1–Ra. Two new hypothetical members of the Act series are proposed to account for irregularities. A relationship is traced between the formula above and the rule of Swinne concerning the initial velocity of α rays. NORRIS F. HALL

The dependence of the range of alpha radiators on the number of component particles in their nuclei. HANS TH. WOLFF. *Physik. Z.* **22**, 352–3(1921); cf. preceding abstr.—On certain assumptions, the range R of most α radiators can be expressed as a function of the no. of the electrons, He nuclei + X_3 particles in their nuclei. $R = \eta_1 (n-0.75n_3)\xi$, where $\eta_1 = 10^\eta$, n = total no. of all particles in nucleus and n_3 = no. of He nuclei (for others see preceding abstr.). Even the simpler formula $R = \eta_1 n \xi$ has certain applications. NORRIS F. HALL

A simple emanation electroscope. An arrangement for the quick determination of the emanation content of radioactive water. P. LUDEWIG. *Physik. Z.* **22**, 298–302 (1921).—By letting the water whose activity is to be measured drop through a channel system in an emanation electroscope, very rapid measurements of its activity can be made with an accuracy of 5–10%. The ionization chamber is connected with a negatively charged Wulf electrometer, the water flows through the ionization chamber and the rate of discharge of the electrometer gives a measure of the emanation content of the water. This method is applicable over a wide range of activity. M. F.

Stationary electron vibrations without radiation resistance. A. D. FOKKER. *Physica* **1**, 107–9(1921).—In this paper, which is wholly theoretical, F. shows how a Bohr atom with electrons revolving in closed paths may be free from radiation resistance without violating the principles of the classical theory. L. H. ADAMS

Ether, light, and matter. OLIVER LODGE. *Phil. Mag.* **41**, 940–3(1921).—L. refers to a paper by B. McLaren (*Phil. Mag.* **26**, 636(1913)) in which gravity is explained by treating matter as a source or sink of ether. This necessitates a universal ether movement, but L. shows that if the motion be irrotational, there is on ordinary theory no resulting effect on waves of light, to the first order of aberration magnitude. There is a second order effect, of the character that appears in the Michelson-Morley expt. L., however, gives other reasons for objecting to the assumption of an irrotational ether movement. He then refers to his own speculation (*C. A.* **15**, 2239) that matter is a sink, as well as a source of radiation, *i. e.*, that matter can be built up out of electro-magnetic fields alone, a view which Eddington (*Proc. Roy. Soc.* (London)

99A, 118(1921)) denies. Finally, he calcs. that thus to generate a mg. of matter would require a beam of sunlight 100 sq. cm. in area, shining for 170 years. R. T. BIRGE

The Einstein spectral line effect. H. J. PRIESTLEY. Univ. of Queensland. *Phil. Mag.* **41**, 747–9(1921).—The predicted Einstein displacement of spectral lines rests on 2 assumptions: (*a*) the atom behaves as a natural clock, giving a value of *ds* which is the same for each vibration, and (*b*) the time period *dt* of a vibration is transmitted by the radiation from the source to the observer. P. gives a proof of the deflection of light in a gravitational field which does not use the principle of least time and other ideas of pre-relativity physics. It is therefore unnecessary to assume (*b*), which follows naturally from the use of the least time principle. Instead it seems more logical to assume that the interval *ds* is transmitted by the radiation. In this case the spectral shift will arise by the transference of the observer, not of the source, to a different gravitational field. R. T. BIRGE

The Einstein spectral shift. OLIVER LODGE. *Phil. Mag.* **41**, 944–5(1921).—L. believes that one step in Priestley's deduction (see preceding abstr.) is open to question, and hence the result is not proved, although it *may* be correct. R. T. B.

The field of an electron on Einstein's theory of gravitation. G. B. JEFFERY. *Proc. Roy. Soc.* (London) **99A**, 123–34(1921).—J. first derives an expression, in polar coördinates, for the line element *ds* of the space surrounding a point which is a singularity both of the elec. and of the gravitational field. Unknown to J., this same expression had previously been derived by Nordström (*Proc. Acad. Sci. Amsterdam* **20**, 1238 (1918)) by applying the calculus of variations to the Hamiltonian function of the combined fields. The present derivation is a direct solution of the field equations. J. next investigates the motion of a particle having both charge and inertia mass in the field just examd. The reaction of the particle on the field is perforce neglected, since no *rigid* solution for a field corresponding to 2 or more singularities has as yet been worked out. All radiation effects are thus omitted, and practically the only usable result is the *approximate* motion of an electron in the neighborhood of an at. nucleus. The orbit thus obtained will be discussed more fully later. It is periodic, but with a rotation of the apse lines. A less approximate solution would probably give *non-periodic* orbits. J. speculates that certain *particular* orbits *might* be periodic, and that these are the "quantized" orbits which all others asymptotically approach. This, if true, would be a complete *explanation of the quantum hypothesis.* The expression for the line element previously deduced can be interpreted as giving to the electron point singularity a radius of the usually calcd. value. Finally, J. derives an expression for the deviation of a ray of light close to a point singularity. The elec. charge brings in an additional term which tends to nullify the usual Einstein deflection. This second term is, however, small, compared to the first, in all cases experimentally possible. Similar conclusions apply to the relativity spectral shift. R. T. BIRGE

Application of the ionization spectrometer to the determination of the structure of minute crystals. W. H. BRAGG. *Proc. Phys. Soc.* (London) **33**, 222–4(1921).—It is shown that crystals in the form of powder can be examd. by the ionization method. The powder is pasted on a flat surface and placed on the spectrometer table in the position ordinarily occupied by the face of a single crystal. A bulb current of 1 milliamp. is sufficient to give satisfactory records. Advantages of this method are: the intensity in different parts of the spectrum can be examd. in detail; each reading occupies only a few secs. and the main part of the spectrum can be run through in half an hr.; it measures relative intensities without further calcn.; and it avoids the difficulty of interpreting the blackening of a photographic plate. The *spectra obtained from Al, Si and LiF powders* when the K series of Rh was used, are given and discussed.

C. C. VAN VOORHIS

Signaling by invisible rays. LOUIS BELL AND NORMAN MARSHALL. *Elec. World* **78,** 307–8(1921).—Brief illus. account of the development of selective transmission and detection of ultra-violet radiation from the W-gas filled incandescent lamp. C. G. F.

Measurement of pole effect and its connection with magnetic separation. H. NAGAOKA. *Astrophys. J.* **53,** 329–38(1921).—A method is outlined for the measurement of minute shifts of spectral lines. A movable slit permits different parts of a source to be observed in rapid succession by means of an echelon or Lummer-Gehrcke plate. Any change in wave length is shown by a displacement of the interference points. By this method a study was made of the pole effect in the iron arc and the results were compared with the magnetic separations of the same lines. In the case of lines showing a positive shift at the pole no correlation was found between pole effect and magnetic separation. For negative pole shifts the correlation was not clearly established but a tendency toward increase of shift with decreasing magnetic separation was observed. The paper is well illustrated by reproductions of spectra photographed by various instruments. K. BURNS

The structure of the bismuth lines. H. NAGAOKA AND Y. SUGIURA. *Astrophys. J.* **53,** 339–48(1921).—The light resulting from the bombarding of Bi by an electronic current was observed by means of a glass Lummer-Gehrcke plate crossed with one of quartz or crossed with an echelon grating. For the line λ4722 the 5 known positive components were confirmed and 7 weak negative satellites were discovered, showing the line to have the general structure common to lines of heavy metals. The principal component is probably multiple, its constituents varying in relative intensity. The line λ4122 has 4 strong components. The line λ4308 consists of 2 principal lines sepd. by 0.350Å, each being a narrow doublet; there are also 2 faint satellites. The authors point out some const. frequency differences and suggest that these may be interpreted in terms of the quantum theory. Well illustrated by spectra. K. BURNS

The arc spectrum of terbium. J. M. EDER. *Sitz. Akad. Wiss. Wien, Abt. IIa* **129,** 421–36(1920).—For a long time the identity of Tb as an element has been in dispute. Its characteristic spectrum, which is strong evidence of its elementary nature, cannot be accurately described, however, until the spectra of the 2 neighboring elements, Gd and Dy, are known. (Cf. *Sitz. Akad. Wiss., Wien, Abt. IIa* **125,** 1467–1535(1916) and *C. A.* **14,** 689.) The spectroscopic work of various early investigators, including Demarcay, de la Fontaine and Urbain, while pointing strongly to the conclusion that Tb is an element, yet left the question in doubt because the materials they used were not sufficiently pure. E.'s own work dates from 1909 when he and E. Valenta began work with a Tb compd. prepd. by Karl Auer v. Welsbach. The latter's later work in sepg. the rare earth elements through many hundreds of fractionations led to the suspicion that not only Tb but perhaps also other elements lie between Gd and Dy. For this reason E. undertook the work of examg. anew the arc spectra of these later Tb prepns. as well as the Gd and Dy fractions from which they were derived. In all, six Tb prepns. were examd. with a large concave grating spectrograph. A comparison of the wave-lengths derived from Auer v. Welsbach's middle fractions (Tb_1, Tb_2, and Tb_2) shows that no new element lies between Gd and Tb. Furthermore, the lines measured by Exner and Haschek and attributed by them to an hypothetical element "E" are shown to be blends to Tb lines with Gd lines of nearly the same wave length. Between Tb and Dy there is evidently a *new element.* A table is given of about 300 lines which are observed in the mixed fractions lying between the purest Tb and purest Dy. In honor of Auer v. Welsbach the name *Welsium* is proposed for the new element A comparison of E.'s results with those derived by Eberhard from Urbain's Tb shows good agreement in general. Inconsistencies between the two are accounted for by the impurities in Urbain's Tb. C. C. KIESS

The Bergmann series of cesium. K. W. MEISSNER. *Ann. Physik* **65**, 378–92 (1921).—Of all the spectral series least is known of the Bergmann series. For the alkalies of high at. wt. many lines of the B-series lie in the region readily observed with dicyanin-bathed plates. With Cs the components of series lines are sepd. sufficiently to permit of precise measurement. A table contg. 29 lines between 6010 Å. and 8079 Å. is given. From lines in this table which are members of the first and second subordinate series frequency differences are computed. The results obtained serve as a criterion of the accuracy of the remaining wave lengths. For lines in the table which are members of the B-series frequencies are also computed. The differences show a progressive decrease as the limit $\Delta\nu = 97.59$ is reached. This suggests an analogy with the 1st subordinate series in which const. $\Delta\nu$ exists between the weaker line of a doublet and a satellite to the principal line. Such satellites were observed for 3 members of the B-series and calcn. proves the expected const. $\Delta\nu = 97.59$ between satellite and weaker line of doublet. However, in B-series the satellite is of shorter wave length than the principal line instead of longer as in first subordinate series. With the precise data given in the wave-length table new series limits are calcd. These represent the observed data within errors of observation. It is proposed that subscripts be assigned to the series letters according to intensity of the lines and not according to the numerical magnitude of the term. Thus a complete doublet of the B-series will be given by $\nu = 3d_1 - mbj$ where $j \geq i$. Sommerfeld's "principle of choice" does not give the correct structure of the doublet unless this scheme of notation is employed. A few Cs lines observed and published in an earlier work are no doubt combination lines of the kind proposed by Paschen and Sommerfeld. They are perhaps emitted only when the source is in a elec. field. C. C. KIESS

4—ELECTROCHEMISTRY

COLIN G. FINK

Electric furnaces: Laboratory types. EZER GRIFFITHS. *Beama* **9**, 145–50(1921); cf. *C. A.* **15**, 3249.—A review. In this instalment C resistor furnaces, the Arsem furnace and high (gas) pressure furnaces are dealt with in detail. Well illustrated. C. G. F.

Molten cast iron held without change in (Baily) electric furnace. F. T. COPE. *Elec. World* **78**, 523(1921).—The tests described indicate that great economies can be obtained by duplexing an elec. resistance furnace of large-hearth capacity with a cupola, melting the heavy scrap and pig Fe in the cupola, discharging this molten metal into the elec. holding (Baily) furnace where it may be refined if necessary, and melting borings and turnings in the holding furnace. The advantage of such a combination is the ability to maintain a uniform pouring temp. so essential in small work, the continuous pouring that is made possible and the fact that borings and turnings may be converted economically into good foundry Fe. C. G. F.

Preparation of sodium sulfide in the electric furnace. L. CAMBI. *Giorn. chim. ind. applicata* **3**, 244–7(1921).—A description is given of the app. employed in the production of Na_2S in the elec. furnace, the process carried out, and tables showing the compn. of the Na_2S produced under different working conditions; also compn. of the material taken out of the furnace at different periods of time during production. C. believes that the process takes place chemically in 3 stages: (I) $Na_2SO_4 + 2C = Na_2S + 2CO_2$. (II) (*a*) $7Na_2S + Na_2SO_4 = 4Na_2O + 4Na_2S_2$; (*b*) $Na_2O + CO_2 = Na_2CO_3$. (III) (*a*) $Na_2CO_3 + 2C = 2Na + 3CO$; (*b*) $2Na + Na_2S_2 = 2Na_2S$. These equations answer closely to the actual conditions frequently encountered in practice. R. S. POSMONTIER

Present and future of the German aluminium industry. ROLAND STERNER-RAINER. *Z. Metallkunde* **13**, 353–67(1921). E. J. C.

Bauxite and alumimiun in 1920. JAMES M. HILL. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part I, 29–36 (Preprint No. 5, published Aug. 31, 1921). E. J. C.

By-product gases of the electrochemical industry. BRUNO WAESER. *Chem. Ztg.* **45**, 74–5, 94–6(1921).—A review. C. G. F.

The electrical engineer in the steel plant and out. F. B. CROSBY. *Assoc. Iron Steel Elec. Eng.* **3**, 351–69(1921). E. J. C.

The formation of hexachlorobenzene in the electrolytic preparation of chlorine. F. BOURION AND C. COURTOIS. *Compt. rend.* **172**, 1365–7(1921).—In the tubes used as Cl collectors have been found yellowish white crystals of C_6Cl_6 with a trace of lower chlorides of benzene. H. W. POST

Electrodeposition of metals: Nickel. W. E. HUGHES. *Beama* **9**, 137–44(1921).—A detailed review. Many literature references are appended. C. G. F.

Nickel and cobalt plating. MAX SCHLÖTTER. *Stahl u. Eisen* **41**, 293–7(1921).—The peeling of nickel plate is due to the adsorption of H and the presence of a certain amount of Fe. The amount of H adsorbed may be considerably lessened by depositing the Ni from a hot soln. At 70–80° Ni takes up only 4.3 times its vol. of H while at ordinary temp. it takes up 13.5 times its vol. Compns. of baths for Ni and Co plating are given and the use of addition agents discussed. R. S. DEAN

Studies of dry batteries. II. F. KAINZ. Vienna. *Chem. Ztg.* **45**, 602–4(1921); cf. *C. A.* **15**, 1657.—*"Behavior of dry batteries during storage."*—K. enumerates some of the common causes of the drop in voltage and states that it would be better to impregnate the C rod with paraffin before using. The drop is a regular and const. function of time, and in normal batteries the efficiency after 7-weeks storage is about 80% of the original, but does not change rapidly thereafter. The rapid deterioration at the start he attributes to the electrolytic soln.-pressure of the Zn ions which at first form complex Zn-NH_3 compds., but later, as this formation becomes slower, the resistance of the electrolyte increases and the potential falls until a time is reached when the Zn is pptd. as $Zn(OH)_2$ and the potential becomes nearly const. *"Attempts to influence the efficiency by changing the compn."*—Very pure MnO_2 increased the voltage by .2–.3 v. More NH_4Cl increased the voltage at first but decreased the storing capacity. CuO was harmful. $MnCl_2$ was no better than NH_4Cl. *"Attempts to increase the storing capacity by different means."*—Pure Zn and better insulation were tried, and K.'s conclusions are that the only soln. of the problem lies in the construction of a battery that can be filled immediately before using. (A battery of this type is on the market now. ED.) J. H. MOORE

High temperature phenomena of tungsten filaments. C. J. SMITHELLS, *et al.* Gen. Elec. Co. London. *Trans. Faraday Soc.* (adv. copy) **1921**, 4 pp.—Two types of W wire are in general use for lamp filaments. One is composed of pure W and the other of W contg. up to 1% of a refractory oxide such as ThO_2. The crystal growth during burning has been investigated for both types. It is shown that the deformation of the filament which occurs during life is a function of crystal growth. Crystal growth which is suppressed in *$W+ThO_2$ filaments*, occurs when the *ThO_2* is reduced. Thoria and other *refractory oxides* can be reduced by *P* (or *Na* vapor) at a high temp. *Chemical reactions* occur *in gas-filled tungsten filament lamps* when traces of the common gases are present. *O* in relatively large quantities, say 1 mm. pressure, rapidly attacks the filament, forming WO_3. Small traces of O form W_2O_5, which is dark blue. The brownish black oxide WO_2 does not appear to be formed by direct combination with O at any pressure. The reaction of water vapor is represented by the reversible equation, $W+nH_2O \rightleftarrows WO_n+nH_2$. The oxide formed at the high temp. parts of the filament is reduced to W by H at the cold parts of the filament in contact with the supports. *CO_2*

attacks the hottest parts of the filament forming a dark blue oxide. *CO* is slowly changed to C and CO_2 at the hottest parts of the filament. *Hydrocarbons* such as methane or vapors from molten paraffin convert the surface of the filament to W carbide. The presence of *Na* gives rise to the reaction, $3\,Na+CO+N=NaCN+Na_2O$, since the A used always contains N and since small quantities of CO are continuously evolved from the hot lamp bulb. In a 60-watt lamp running at normal temp. and through which a current of CO, N and Na vapor was passed, 0.5 g. of *NaCN* was formed in 100 hrs. Photomicrographs are shown. D. MACRAE

Vacuum tubes used as detectors of electrical oscillations. L. HARTSHORN AND E. S. KEEPING. *Proc. Phys. Soc.* (London) **33**, 249–58(1921).—The development is described of a robust form of vacuum tube which was used as a detector of elec. oscillation in the "wireless" circuits carried by airplanes. Sealed-in electrodes are avoided, being replaced by strips of tinfoil (around the outside of the tube), to which contact may be made by the spring clips holding the tube in position. When a discharge is once passed through such a tube, thenceforth it is much easier to get a discharge to pass. The change produced by the first discharge is annulled by heating the tube above 210°. Further, if the walls are coated on the inside with a metallic film, this first discharge is unnecessary, and the tube is unaffected by heating, but when the walls are coated with an insulator it is, if anything, more difficult to pass a discharge. A silica tube behaves like one coated with metal. It is suggested that the change in the tube may be due to the formation of a layer of gas mols. on the walls by the first discharge, but this does not explain the behavior of the silica tube. C. C. V.

Economy of substituting copper for iron wire. H. S. RUSH. *Elec. World* **78**, 515–7(1921); 5 illus.—Report of investigations of elec. losses in Fe and steel conductors, to det. conditions under which it is essential to adopt Cu. C. G. F.

Signaling by invisible rays (BELL, MARSHALL) **3.** Developments in nitrogen fixation (HARKER) **18.** Waterwheel test by chemical means (STARR) **13.** Relative values of protective metallic coatings for iron and steel (COWPER-COLES) **9.** Determination of water in oils for transformers (RENGADE, CLOSTRE) **7.** Rust-proof piano wire, springs, tools, etc. (U. S. pat. 1,383,174) **9.** Agglomerating carbon or other materials (U. S. pat. 1,381,748) **18.**

Storage battery. W. C. BROOKS. U. S. 1,381,399, June 14, Structural features.

Storage battery. A. J. BARACREE. U. S. 1,381,959, June 21. Structural features.

Storage battery. A. BUGBEE. U. S. 1,382,270, June 21. The battery container is formed of an integral piece of hard porcelain having several chambers.

Storage batteries. A. H. SNYDER. Can. 212,304, June 28, 1921.

Storage battery plates. K. WRIGHT. U. S. 1,381,387, June 14. In forming tanks for making battery plates, there is used at the negative pole a series of connected pasted plates, and at the positive pole a series of connected dummy Pb blanks is used. The negative plates are electrolyzed to form them.

Electric battery. E. R. GILL. U. S. 1,381,298, June 14. Structural features.

Decomposition of alkaline chloride solutions by means of electrolysis. K. HEINEMANN. Can. 212,061, May 31, 1921. In an electrolysis process for decompg. alkali chloride solns. by means of a Hg cathode and a porous diaphragm sepg. the electrodes, the electrolyte is circulated from one compartment of the cell to the other, thence to the satg. device.

The production of alkalies and chlorine by means of mercury cathodes. K. HEINEMANN. Can. 212,060, May 31, 1921. In cells for electrolytically decomposing alkali chloride solns. by means of a flowing Hg cathode, a stationary, horizontal plate

is provided with impediments on its surface forming right angles with the direction of flow of the Hg. The Hg surface is thus kept in continuous agitation.

Producing solid peroxides. W. WEBER. Can. 212,158, May 31, 1921. In the electrolytic production of solid peroxides such sol. compds. are added to the electrolyte as will form with the H_2O_2 formed at the cathode insol. compds. O or O-contg. gases are introduced into the cell.

Apparatus for the electrolytic decomposition of anhydrous magnesium chloride. EDGAR A. ASHCROFT. Can. 212,503, July 19, 1921.

Electrolytic apparatus for deposition of metals. M. M. MERRITT. U. S. 1,381,882, June 14. The app. has a revolving cylindrical cathode drum and is adapted for manuf. of electrolytic sheet Cu.

Electrolytic apparatus adapted for manufacture of copper wire. M. M. MERRITT. U. S. 1,381,883, June 14.

Electrolytic condensers. C. L. FORTESCUE. U. S. 1,382,899, June 28. Structural features.

Electric furnaces. E. W. HUGHES. Can. 212,329, July 5, 1921. The metal shell of the furnace has a refractory lining, the outer surface of which has an offset therein which forms a gap between the inner face of the shell and the outer face of the lining for the circulation of a cooling medium to carry off the heat radiating from the lining.

Electric furnaces. H. A. GREAVES. Can. 212,321, July 5, 1921. In an elec. furnace installation having sets by transformer windings the connections are such that an inversion of polarity or a rotation of phase may be effected so that the current transmitted by the hearth can be varied over a wide range.

Electric furnace and method of operation. L. C. H. GROEGER. Can. 212,618, July 26, 1921. A furnace has a pair of swinging adjustable side electrodes located directly on opposite sides of a heating chamber; an adjustable upper electrode depending through the top wall of the chamber; a source of elec. energy and means whereby either the side electrodes or the upper electrode may be caused to operate through the bath in the chamber, completing the circuit through a hearth terminal.

Sintering phosphatic materials. F. S. WASHBURN. Can. 212,558, July 19, 1921. A mixt. of phosphate rock and silicious material is sintered to form a porous mass which, with C, is charged into an elec. furnace and heated to drive off the P. The C may be sintered with the other ingredients and form part of the porous mass.

Silicon carbide. H. E. SCHABACKER. U. S. 1,381,346, June 14. A mixt. of sand and pitch coke is used for producing a relatively pure Si carbide.

Preparation of crude material for the manufacture of calcium carbide. F. L. SLOCUM. Can. 180,801, Dec. 4, 1917. A hydrate of a metal and a carbonaceous material is coked at a temp. which will remove the volatile matter and water of hydration, then the mass is briqueted in an elec. furnace. Specifically, peat is mixed with a hydrate and coked. Or moist peat can be mixed with a metal oxide; the latter becomes hydrated, drying the peat before coking.

Apparatus for making carbides. J. H. REID. Can. 180,785, Dec. 4, 1917. Electrodes are placed in combination with means for feeding material to and between them and a support or hearth which retains material not fully converted within the zone of reaction until conversion is completed and which provides for the continuous flow of the converted product from the zone of reaction. Means are specified for varying the position of the zone of reaction with respect to the material in order that arcing may be prevented.

Alloy filament. ALADAR PACZ. Can. 212,669, July 26, 1921. A filament for incandescent lamps consists of W with a small percentage of Zr.

7—ANALYTICAL CHEMISTRY

WILLIAM T. HALL,

Physico-chemical volumetric analysis. R. DUBRISAY. *Ann. fals.* **14,** 9–18(1921).—Outline of the purpose and scope of physico-chem. analysis and of D.'s previous work on the subject. (Cf. *C. A.* **7,** 2169; **8,** 2660; **9,** 504; **12,** 1355; **13,** 392, 689; **14,** 2433, 2742; **15,** 353.) A. P.-C.

Selection of analysts for color work in chemistry. H. R. O'BRIEN. *Bur. Mines Repts. Invest.* No. **2268,** 5 pp.(1921).—To det. what operators were best qualified to carry out the Haldane carmine detn. of CO in blood, a series of similar colors were prepd. in pairs to correspond to larger and smaller differences in the CO content. The tests were tried on some 25 operators and in this way the norm for the lab. was detd. as well as the operators most skilful in detecting slight differences in the shades. W. T. H.

Kieselguhr for retaining precipitates. G. BRUHNS. *Z. angew. Chem.* **34,** Aufsatzteil, 242–3(1921).—Instead of using a newly described filter paper into which kieselguhr has been incorporated, and which is relatively brittle, it is recommended that ordinary filter papers be prepd. for retaining fine ppts. by adding kieselguhr to water and running this through the filter before the main filtration is carried out. Kieselguhr holds back only solid suspensions, and it is not necessary to mix it beforehand with the liquid to be filtered. It is not well adapted to removing coloring matters. W. C. EBAUGH

Kieselguhr for retaining precipitates. ZINKEISEN. *Z. angew. Chem.* **34,** Aufsatzteil, 356(1921).—Adding to Bruhns' statements (cf. preceding abstr.) concerning the property of kieselguhr to remove solid suspensions, it ought to be said that it can also remove oily substances, as shown by its use in filtering water contg. terpenes from lemon skins. W. C. EBAUGH

The analysis of phosphor bronze. A simplified method of determining phosphorus. E. D. GARCIA. *Anales soc. quim. Argentina* **8,** 104–5(1920).—The sample is dissolved in HCl with the aid of $KClO_3$, boiled to expel Cl_2, diluted, pptd. by H_2S, and filtered. The filtrate is boiled with a little HNO_3, and then an amt. of aluminium sulfate equal to 2–3 times the wt. of sample taken is added. When solution is complete a slight excess of NH_4OH is added, the mixture is then boiled and filtered and the ppt. is washed free from chlorides. The ppt. will contain all the P from the sample as $AlPO_4$. The ppt. is dissolved in dil. HNO_3 and the P detd. by the usual molybdate method. L. E. G.

Theoretical considerations on the determination of the phosphorus content of steels. Separation of phosphorus from the other components of steel. R. ARIANO. R. Politecnico, Turin. *Gazz. chim. ital.* **51,** I, 1–31(1921).—This paper although it contains no new methods constitutes a clear presentation of the subject and gives many interesting comments upon the various known methods. E. J. WITZEMANN

Gravimetric methods of analysis. XVIII. L. W. WINKLER. *Z. angew. Chem.* **34,** Aufsatzteil, 383–4(1921).—XXIII. *Determination of cadmium.*—In the presence of H_2SO_4 and a very little HCl, a red ppt. of nearly pure CdS can be obtained which has a constant and definite wt. when dried at 130° although it contains 1% of SO_4. If much HCl or HNO_3 is present it should be removed by evapn. with H_2SO_4. To 100 cc. of soln. contg. 0.01–0.25 g. of Cd, add 1 drop of *N* HCl and 3 cc. of cond. H_2SO_4. Heat the soln. to boiling in a 150-cc. Erlenmeyer flask and conduct H_2S into it for 15 min. Then place the flask in cold water and continue the stream of H_2S for 15 min. longer. Close the flash with a stopper and allow it to stand overnight. Filter through a cup-shaped funnel contg. a wad of cotton wool, by using suction and washing with 50

cc. of cold water contg. a drop of AcOH and some H_2S. Remove the funnel from the suction and, as a final washing, pour a few drops of MeOH upon it; the ppt. will run through if suction is now applied. Dry at 130° for 1 hr. Add 1 mg. to the wt. obtained and multiply by 0.9806 to get the wt. of pure CdS. If HCl or HNO_3 is present in the original soln., evap. with 3 cc. of cond. H_2SO_4, then add 1 drop of *N* HCl and treat as described. If Zn is present in the soln. some of it is likely to be pptd. with the Cd. Dissolve the ppt. in HCl, add 3 cc. of cond. H_2SO_4, evap. to fumes, add 1 cc. of *N* HCl and reppt. the Cd as CdS. W. T. HALL

The determination of small quantities of zinc. M. BODANSKY. *J. Ind. Eng. Chem.* **13**, 696–7(1921).—In a study of the Zn content of marine organisms a turbidometric method was used which was based upon previous recommendations of Breyer and of Birckner. The weighed material was oxidized and decomposed by the Gautier method and the ash digested with hot, dil. HCl. After filtering, the extract was evapd. to dryness and the residue dissolved in 2 cc. cond. HCl and 50 cc. of water. The Cu was pptd. as CuS and the filtrate boiled to expel H_2S. It was then cooled, neutralized with NH_4OH and treated with 10 cc. of 50% citric acid soln. After heating to boiling $CaCO_3$ was added, if necessary, to form about 1 g. of Ca citrate ppt. A rapid stream of H_2S was next introduced until the liquid was cold. After some hrs. the ppt. was collected on a filter, washed with 2% NH_4CNS soln. and dissolved back into the original flask. If a red color of $Fe(CNS)_3$ was obtained at this stage the pptn. of the Zn as ZnS was repeated. The dil. soln., or an aliquot part, was placed in a Nessler tube and 5 cc. of $K_4Fe(CN)_6$ soln. (34.8 g. per liter) added. The turbidity was compared with that obtained similarly with known quantities of Zn. W. T. HALL

A simple method for the determination of vanadium in ores and metallurgical products. R. B. SCHAAL. *J. Ind. Eng. Chem.* **13**, 698–9(1921).—Without the removal of other constituents, the soln. of the material is evapd. repeatedly with HCl to reduce all the V to the quadrivalent condition until at the end a vol. of 10 cc. is obtained. This is diluted with 60 cc. of water and the filtered soln. is treated with 60 cc. of 15% $(NH_4)_2HPO_4$ soln. and with NH_4OH until a bulky ppt. of $FePO_4$ appears. This is dissolved by 7.5 *N* HCl and, if a highly colored soln. results, 10 cc. of 18 *N* H_2SO_4 are added. In some cases it is necessary to repeat the treatment with phosphate and H_2SO_4. The soln. is then diluted to 300 cc. and titrated with permanganate until the V is again in the quinquevalent condition. W. T. H.

The volumetric determination of mercury. EINAR BIILMANN AND KARIN THAULOW. *Bull. soc. chim.* **29**, 587–92(1921).—Two methods are described, both depending upon the tendency of Hg to form complex ions. (1) *Detn. by means of allyl alcohol.*—Allyl alc. reacts with a salt of Hg as follows: $C_3H_5OH+Hg(OAc)_2 \longrightarrow C_3H_5OHgOAc+HOAc$. In the soln. the conc. of Hg^{++} is about $10^{-3.4}$. The base, C_3H_5OHgOH, corresponding to the complex salt is so weak that it does not affect phenolphthalein indicator and is set free when the salt is treated with stronger bases. If the base is treated with KBr a complex bromide is formed and the liberated OH^- ions correspond to the quantity of Hg present. These facts are expressed by the following equations: $C_3H_5OHgOAc+NaOH \longrightarrow C_3H_5OHgOH+NaCl$; $C_3H_5OHgOH+KBr \longrightarrow C_3H_5OHgBr+KOH$. To show that a satisfactory detn. of Hg could be made, about 0.6 g. of HgO were dissolved in an excess of H_2SO_4 or AcOH, the soln. was dild. with water free from CO_2, 2 or 3 cc. of C_3H_5OH were added and a little phenolphthalein. Dil. NaOH was added until a red color was obtained and then 0.2 *N* H_2SO_4 to decolorization. 5 g. of KBr were added to form the complex bromide and the liberated alkali was titrated with 0.2 *N* H_2SO_4. Excellent results were obtained. (2) *Detn. with KI.*—HgO is neutral to phenolphthalein but it reacts with KI and H_2O to form the sol. but slightly ionized iodide. $HgO+2KI+H_2O \longrightarrow HgI_2+2KOH$. An accurate volumetric detn. of Hg can be accomplished as follows: To the soln.

of the acetate or sulfate in the presence of excess acid, but in the absence of chloride or CO_2 add phenolphthalein and an excess of NaOH to ppt. HgO. Neutralize the excess of alkali by carefully adding dil. H_2SO_4, until the red color due to the indicator disappears, and a few g. of KI. Stopper the Erlenmeyer flask and after all the HgO has dissolved, titrate with standard acid. W. T. HALL

Gas volumetric determination of aluminium. L. LOSANA. *Giorn. chim. ind. applicata* **3**, 239–41(1921).—The Al content of an alloy containing 65% or more of Al can be detd. with remarkable accuracy by measuring the vol. of H_2 evolved by treatment with KOH soln. The presence of Mg has been found to interfere but the detn. can be accomplished in the presence of Zn or small quantities of Si. Place 0.2 g. of borings in a 200-cc. Erlenmeyer flask which is fitted with a stopper carrying a drop funnel for introducing the alkali soln., and a glass delivery tube leading to a pneumatic trough. Add 30 cc. of boiled water, stopper the flask, partly fill the supply funnel with water to exclude air, close its stopcock and place 15 cc. of 20% KOH soln. in the funnel. Boil the water in the flask until no more air bubbles are evolved during a period of 5 min. Then place a gas buret filled with water over the tubing where it ends in the trough, remove the flame and stop the water from sucking back from the trough into the flask by means of a pinch cock placed on rubber tubing between 2 branches of the delivery tube. Allow most of the KOH soln. to flow into the flask, quickly apply heat and open the pinch cock. Boil until no more bubles of H_2 are evolved and measure the vol. with the usual precautions. ROBERT S. POSMONTIER

The detection of antimony in the presence of tin. VLADIMIR NJEGOVAN. *Chem. Ztg.* **45**, 681(1921).—The test depends upon the pptn. of an oxysulfide of Sb by means of $Na_2S_2O_3$. To the HCl soln. add soda until nearly neutral but avoid pptn. Add 1 or 2 drops of 0.5 *N* $Na_2S_2O_3$ soln. and boil 1 min. If a red or reddish yellow ppt. of Sb_2OS_2 is formed, Sb is present. A white ppt. of S shows that Sb is absent. If CuS is formed, add soda until an alkaline reaction is obtained. This causes the Sb ppt. to dissolve but the CuS remains unattacked. Boil, filter and make the filtrate acid to cause repptn. of Sb_2OS_2 upon further boiling. W. T. H.

Rapid determination of silver in alloys by means of a modified silver chloride method. SAUERLAND. *Chem. Ztg.* **45**, 735–6(1921).—Dissolve 0.5–1 g. of alloy in 10 cc. of cond. HNO_3, a covered 200-cc. beaker being used. After the metal is completely attacked, add a few drops of water and boil to cause pptn. of Au, Sn and Sb if present. Dil. to 75 cc., boil again and filter if necessary after 5 min. To the clear soln. add dil. HCl with stirring until no more AgCl forms. Heat to boiling and filter off the coagulated AgCl, an ashless filter being used. After washing with hot water, place the filter in a small crucible (such as is commonly used for parting a button of Au-Ag) with the apex of the filter touching the bottom of the crucible and the top of the open filter extending above the crucible. Heat carefully with a small flame beneath the crucible and with a smaller stream of illuminating gas playing upon the ppt. The flame from the latter should be about 4 cm. long. In this way the ppt. of AgCl is reduced to Ag before it has a chance to melt. After 10 min. the reduction should be complete whereupon the Ag can be heated until the mass sinters together, detached from the crucible and weighed. In the analysis of Au alloys it is not always possible to dissolve out the Ag by treatment with HNO_3. In such cases it is well to heat the sample with twice as much Zn or Cd under a cover of KCN; in this way a decomposable alloy is formed. W. T. HALL

The determination of small quantities of iron. L. MAQUENNE. *Bull. soc. chim.* **29**, 585–7(1921).—The test described has been found useful for estimating the Fe content of various vegetable substances. Take 0.01–0.05 g. of the ash obtained by careful ignition to dull redness, moisten with HNO_3 and again heat to destroy residual carbonaceous matter, add 1 cc. of 10% H_2SO_4, evap. gently to fumes, add 3 drops HCl, dil.

with 1 cc. of water and decant into a small centrifuge tube of about 4 cc. capacity. If $CaSO_4$ is in suspension, centrifuge and decant off the clear liquid. To this add a few drops of Na_2HPO_4 soln., enough NH_4OH to give a slight permanent ppt. and AcOH to dissolve all of this except $FePO_4$. Centrifuge and make sure by testing with $K_4Fe(CN)_6$ that the clear liquid now obtained, and which is to be discarded, contains no Fe. Dissolve the ppt. in 3 drops of HCl, dil. with 2 cc. of water and pour the soln. into a similar tube contg. a few drops of freshly prepared $K_4Fe(CN)_6$ soln. Compare the color with that obtained similarly with solns. of known Fe content. 1 drop of a soln. contg. only 0.0025 mg. of Fe will give the test. Test all residues and ppts. for Fe by heating with 3 drops of HCl and adding 2 cc. of water and make allowance for any Fe thus found. W. T. HALL

Colorimetric determination of sulfur in steel. G. MISSON. *Ann. chim. anal. chim. appl.* **3**, 200–1(1921).—Place 1 g. of the borings in a thick conical flask about 10 cm. tall and 8 cm. in diam., add 10 cc. of gasoline, *d.* 0.71 and 50 cc. of HCl, *d.* 1.14. Cover the mouth of the flask with filter paper which has been impregnated with $AsCl_3$ soln. by the following treatment: Mix 10 g. of As_2O_3 with 30 cc. of cond. HCl, stir, add 500 cc. of boiling water and heat till all the solid has dissolved. Dil. to 1 liter and wet the filter paper with it. Place the paper on stirring rods to drain and while still damp, cut into strips each 10 sq. cm. in size. Keep the paper moist. After placing such a strip of impregnated paper over the flask, cover this with a piece of thin felt (5 mm. thick) of the same size and similar disks of ebonite and sheet lead. At the end of about an hr. compare the density of the As_2S_3 ppt. produced on the impregnated paper disk with that obtained similarly with standard steels of known S content. In a French lab. about 100 detns. per day are made in this way. The results are good. W. T. H.

A rapid method for the determination of arsenic in arsenates. JAMES M. BELL. *J. Elisha Mitchell Sci. Soc.* **35**, Nos. 3 and 4, 90–1(1920).—The method described is similar to that used by Gooch and others and depends upon the iodometric titration of arsenite to arsenate in barely acid soln. to which about 5 g. of Na_2HPO_4 are added. The arsenate is reduced to arsenite by treatment with KI in 2 *N* HCl soln. H. W. E.

The estimation and detection of arsenic in poisoning cases. J. S. JAMIESON. *J. S. African Assoc. Anal. Chem.* **4**, No. 2, 9–15(1921).—Interesting details are given of experiences in toxicological work. The Reinsch test has proved useful for the detection of As and Gautier's method of destroying organic matter by treatment with HNO_3 and H_2SO_4 is better than other methods of accomplishing the same purpose. In the examn. of human viscera, however, there is a loss of about 20% of the total As during this treatment but corresponding losses are more serious with other methods. For the quantitative detn. of As the iodometric method of H. H. Green is preferred but in this method 10% H_2SO_4 seems better than the 30% acid. W. T. H.

Determination of sulfur in roasted pyrites. RUDOLF SIEBER. Kramfors. *Zellstoff u. Papier* **1**, 75–7(1921).—Comparative expts. in which the Lunge-Stierlin and the List methods were used, showed that the same result was obtained by either method. The 1st method is somewhat shorter if the ppt. from the melt is washed on a Büchner funnel, which contains a layer of ignited kieselguhr, until approx. 200 cc. of filtrate are obtained. C. J. W.

A new method for the determination of thiosulfates in the presence of sulfite and for the determination of tetrathionate. ALBIN KURTENACKER AND ALBERT FRITSCH. *Z. anorg. allgem. Chem.* **117**, 262–6(1921).—By titration with I in slightly acid soln. the thiosulfate is changed to tetrathionate and the sulfite to sulfate. Then by treatment with KCN, the following reaction takes place $KCN+Na_2S_4O_6+2NH_4OH=KCNS+(NH_4)_2SO_4+Na_2S_2O_3+H_2O$ and the thiosulfate thus formed can be titrated with I soln. In carrying out the analysis, first det. the vol. of standard I soln. required to

change the thiosulfate to tetrathionate and the sulfite to sulfate in the presence of very dil. H_2SO_4. Then dil. to approx. 200 cc., add phenolphthalein indicator soln. and neutralize with 5% NH_3 soln. Add 7 cc. of 10% KCN soln. and after allowing 15 min. for the desired reaction to complete itself, add 25–50 cc. of 9 *N* H_2SO_4 and titrate again with 0.1 *N* I soln. W. T. H.

The determination of small quantities of hydrocyanic acid in viscera and its disappearance during decomposition. J. LEWIS. *J. S. African Assoc. Anal. Chem.* **4**, No. 2, 19–22(1921).—After trial of several methods of analysis it was found that titration with $AgNO_3$ of the distillate from the acidified material gave the best results but it is necessary to remove H_2S by conversion to PbS and redistg. off the HCN. To prevent frothing, 50 cc. of alc. was added to the contents of the distg. flask. During the decompn. of the viscera the loss of HCN was found to take place very rapidly and with unpreserved viscera all may be lost in less than 2 days. When the viscera are preserved in alc., a slow progressive loss takes place but over half the original quantity of HCN remains at the end of 30 days. W. T. H.

Reactions for hydrocyanic acid. THURE SUNDBERG. *Svensk Kem. Tids.* **33**, 112–3(1921).—The sensitiveness of the tests for HCN was investigated. In the Prussian blue test the substitution of Na_2CO_3 or Na_2HCO_3 for NaOH made the reaction more delicate. The guaiacum test was improved by the following prepn: 0.1 g. guaiacum resin dissolved in 50 cc. 95% EtOH is made up fresh for the day's tests and mixed with 1:1000 $CuSO_4$ soln. in the proportion 10:3. The sample to be tested is placed in an Erlenmeyer flask and in the mouth of the flask is placed a strip of filter paper which has been moistened by the reagent. This paper is held in place by a stopper. The paper is colored blue by minute amts. of HCN. 0.001 mg. in 10 cc. water gave a reaction in 3 min. A. R. ROSE

Use of "fornitral" for the detection and estimation of nitric acid. ANON. *Ann. chim. anal. chim. appl.* **3**, 207–8(1921).—Fornitral contains 2 mols. of HCO_2H united with endoanilo-diphenyl-dihydro-triazole. The substance is very sol. in water with a distinct acid reaction and the 10% soln. is more stable than a soln. of nitron which it is proposed to displace. The salts of fornitral with the following acids dissolve with increasing difficulty, the numbers representing cc. of water required to dissolve 1 g. of salt: HBr, 300; $HClO_3$, 400; HNO_2, 4,000; $H_2Cr_2O_7$, 6,000; HCNS, 15,000; $HClO_4$, 50,000; HNO_3 60,000 at 15° and 80,000 at 0°. The soly. of the nitrate is much less in the presence of an excess of fornitral. The picrate is less sol. than the nitrate and quite a number of organic nitro derivatives also yield insol. ppts. For the detn. of HNO_3 the soln. analyzed should contain about 0.1 g. of the acid in 100 cc. Add 10 drops of dil. H_2SO_4, heat nearly to boiling and treat with 10 cc. of the reagent. Cool and allow to stand 2 hr. at about 0°. Filter through a gooch, Neubauer or alundum crucible, wash with a little cold water (12 cc. added in 3 portions), dry at 110° for an hr. and weigh. The ppt. contains 16.8% of HNO_3. W. T. HALL

Detection of methanol in liquors and spirits. L. HOTON. Liège. *Ann. fals.* **13**, 490–1(1920).—A 250-cc. portion of the liquor contg. at least 20% by vol. of alc. is placed in a distn. flask and heated, and as soon as the boiling begins the flame is lowered so that distn. proceeds at the rate of about 10 drops a min. The neck of the flask is provided with 2 bulbs filled with glass beads (a Lebel-Hemminger distn. head is quite suitable), and with a thermometer divided in 0.2°. The temp. is noted when it becomes about const., *i. e.*, about 0.5 min. after condensation begins in the neck. A temp. of 78° proves the absence of a fraudulent addition of MeOH, which would lower the temp. The method is only sensitive to about 2.5% MeOH; but in practice when MeOH is added fraudulently it is always present in larger quantities than this. A. P.-C.

Method for determining the finer dust particles in air. A. L. MEYER. Johns

Hopkins Univ. *J. Ind. Hyg.* **3**, 51–6(1921).—A Luer syringe graduated to 100 cc. but with a capacity of approx. 160 cc. is thoroughly cleaned with soap and water, and alc. It is rinsed with freshly distd. water, and filled with distd. water free from air bubbles. This water is then forced completely out; 20 cc. of distd. water are drawn into the syringe from a flask provided with a filter of cotton-wool. The air sample is now taken by withdrawing the piston sufficiently to admit approx. 100 cc., the exact vol. admitted from the graduation being read. A piece of rubber membrane is placed over the nozzle and held tightly with the finger; the syringe is shaken vigorously for 1 min. with an up and down motion, then is held in a vertical position, while the water is brought to the very top of the nozzle and then withdrawn slightly to admit a small bubble of air. The latter manipulation catches and brings into suspension any particles which have adhered to the narrow region of the nozzle. One drop of the liquid is permitted to flow from the syringe into the chamber of a Levy blood counting app. using the metal connecting piece; and the particles are counted by oblique illumination. The particles must be permitted to settle before counting. The entire number of particles in 2 fields, each 1 sq. mm., are counted; and the av. value is used in the calcn. Agglomeration of the particles was not noted. Strict attention to cleanliness of the syringe and of the counting app. was essential. Consistent results were obtained. A modified form of the dust collecting app. is also described. JOSEPH S. HEPBURN

The determination of water in oils for transformers. ETIENNE RENGADE AND JEAN CLOSTRE. *Compt. rend.* **173**, 311–13(1921).—A small quantity of moisture in oils for this purpose is very objectional and as the water is dissolved to a slight extent by the oil it is not easy to carry out the test. Such tests as that with anhydrous $CuSO_4$ have proved unsatisfactory. The proposed method depends upon the volatilization of the water by means of a current of hot dry air and then condensing it by means of liquid air or solid CO_2, weighing each condensate and testing to see whether it is oil or water. In one case although water was not found to any extent, the oil was found useless because of a high content of volatile oil. To carry out the test place 200 cc. of oil in a short-necked, round-bottomed flask closed by a stopper carrying a thermometer and tubes for the entrance and exit of an air stream. The latter tube is bent sharply and is connected by rubber tubing with a condenser tube the orifice of which is a short distance from the neck of the flask. Immerse the flask in an oil bath heated to 80° and surround the bath and connections with an envelope of asbestos paper to prevent any condensation before the condenser is reached at the rate of 20 liters per hr., draw air dried by H_2SO_4 and P_2O_5 through the oil and change the receiving flask every 15 min., the gain in wt. being detd. in each case. The presence of water in the condensate can be detd. by its freezing at 0°, by the way it condenses in the tube, by the $CuSO_4$ test or by the reaction with the double iodide of Pb and K which is turned yellow by water. The presence of oil is characterized by its not freezing at 0° and by its inflammability. W. T. HALL

A new reaction of ammonia. CONST. D. ZENGHELIS. *Compt. rend.* **173**, 153–5 (1921).—The test depends upon the formation of a mirror of Ag when a soln. of $AgNO_3$ and methylal comes in contact with NH_3. The reagent is a 20% soln. of $AgNO_3$ mixed with 3 parts of commercial 33–35% methylal. The reagent should be heated before trying the test. A slight pulverulent deposit does no harm. The soln. is stable for about 2 hr. A few drops of the reagent on a small watch glass placed near 0.5 cc. of *N* NH_4OH soln. and covered with a small crystg. dish will show the mirror within 30 sec. To a soln. suspected of contg. NH_3 or an NH_4 salt, add NaOH or Na_2CO_3 until alkaline and place 0.5 to 1 cc. in a 12-cm. test-tube. On top of the test-tube place a small watch glass with the convex surface down and raised by a bit of stirring rod to permit the escape of gases. Place a small drop of reagent on a rod near this opening and add

a little cold water on top of the watch glass to act as a condenser. Heat the contents of the test-tube until drops of moisture begin to condense on the watch glass and on the rod with the reagent. Mirrors were obtained by this procedure with only 3.4×10^{-7} g. of NH_3. To detect NH_3 in a large vol. of soln., add H_2SO_4 and evap. to 0.5 cc. Then add Na_2CO_3 and apply the test. W. T. H.

Detection of nitrogen in organic compounds. CONSTANTIN D. ZENGHELIS. *Compt. rend.* **173**, 308–10(1921).—This test, which is believed to be much more sensitive than the usual test for ferrocyanide after decompn. with Na, depends upon the decompn. of the substance with soda lime and finely divided Cu whereby the N of the org. material is converted into NH_3 which is identified by the formation of a mirror of Ag when the gas comes in contact with a soln. of $AgNO_3$ and methanal. (See preceding abstract.) In a porcelain crucible, mix a small quantity of the organic substance with 2 parts of dry soda lime and 1 part of finely divided, electrolytic Cu. Cover with more of this mixt. and place over the crucible a small watch glass and near it a drop of the reagent. Heat the crucible on a sand bath or quartz-plate over a small flame. After 1 or 2 min. a drop of water will condense on the watch glass and if N is present enough NH_3 will be evolved to give the Ag mirror. To detect N in a low-boiling liquid, or in a substance which decomposes below 150°, a somewhat different procedure is recommended. Use a glass tube 20 cm. long and sealed at one end instead of the crucible. At the closed end place a little sugar, a short layer of soda lime and Cu mixt., then the substance mixed with soda lime and finely divided Cu and finally a layer of soda lime and Cu without any organic substance. Close the tube with a stopper carrying a small piece of glass tubing bent at a right angle. Just below the outside opening of this tubing, place a watch glass and a drop of the reagent. With the tube in a horizontal position, heat its contents by beginning with the front end and ending at the sugar, the combustion of which serves to expel all NH_3 from the tube. W. T. HALL

Determination of cresol (CHAPIN) **11B.** Cleaning and keeping clean volumetric apparatus (BERG) **1.**

Determination of carbon in ferrous metals. W. F. FINKL. U. S. 1,382,072, June 21. In the detn. of C in ferrous metals, the CO_2 evolved from the C in the metal is absorbed by a dry physical mixt. of KOH and NaOH and asbestos or by a similar mixt. of an alkali metal hydroxide and a fibrous material. The use of an absorbent of this character serves to provide a large contact surface for the absorption.

8—MINERALOGICAL AND GEOLOGICAL CHEMISTRY

EDGAR T. WHERRY AND WALTER F. HUNT

Recent advances in science—Mineralogy. ALEXANDER SCOTT. *Science Progress* **16**, 20–2(1921).—Review of recent work on the synthesis of minerals. J. S. H.

A new antimoniferous bismuth sulfide mineral. S. PIÑA DE RÚBIES. *Anales soc. españ. fis. quim.* **18**, 335–8(1920).—This new mineral is found associated with oruetite (*C. A.* **13**, 2835, 3117) which it resembles. Its hardness is 2 and its sp. gr. is 6.8; its structure is fibrous, and it is unusual in being an excellent conductor of electricity. Quant. analysis leads to the formula: $8Bi_2S_3.Sb_2S_3.Bi_2(Se, Te)_3$. L. E. G.

Galenobismutite from a gold-quartz vein in Boise County, Idaho. EARL V. SHANNON. *J. Wash. Acad. Sci.* **11**, 298–300(1921).—The specimen examd. was from the Belzazzar Mine dump, Quartzburg district and occurs interstitially in a quartz vein. It is clearly the youngest mineral of the vein. Color, light gray tarnishing to yellow. In general appearance it resembles bismuthinite. H = 2.5. Analysis gave Pb 23.93,

Fe 0.39, Cu 1.73, Sb 2.56, Bi 53.59, S(calcd.) 17.80%, leading to the formula $PbBi_2S_4$ or $PbS.\ Bi_2S_3$. L. W. RIGGS

Aphthitalite from Kilauea. H. S. WASHINGTON AND H. E. MERWIN. Geophys. Lab. *Am. Mineral.* **6**, 121–5(1921).—Data are given as to the occurrence, physical and optical properties of the mineral. Its *n*s. are rather low: $\omega = 1.487$, $\epsilon = 1.492$. In crystallography and optical properties there is a close relationship and gradual transition from arcanite (K_2SO_4) through aphthitalite to thenardite (Na_2SO_4). Analysis gave: SO_3 51.50, Cl 0.03, K_2O 23.72, Na_2O 22.76, CaO 0.39, MgO none, CuO 0.46, H_2O 0.25, insol. 0.76, sum 99.87%. This corresponds to K_2SO_4 43.88, Na_2SO_4 52.12%, and on comparison with other analyses, it is found that in Na ratio it is exceeded by but one other occurrence, that from Etna. No Pb could be detected, and it is noteworthy that the lava is of Na-Ca type, while that at Vesuvius, whose aphthitalite carries Pb, is highly potassic. Aphthitalite has been regarded as a definite double salt, $3K_2SO_4.Na_2SO_4$, but the exptl. evidence of Van't Hoff and the finding of these high-Na specimens at Etna and Kilauea favor the view that it is an isomorphous solid soln. The Cu is evidently present as $CuSO_4$, which is isomorphous with aphthitalite and the alk. sulfates, and which, while stated in the books to be colorless or gray, is decidedly greenish blue when moistened with a liquid of the same mean *n*. The formation of aphthitalite at Etna has been ascribed to the action of SO_3 on chlorides, but at Kilauea there is little Cl, and it is suggested that it was more probably formed by volatilization of the alkalies and Cu as sulfides, which oxidized on contact with the air. E. T. W.

Mineral resources of Alaska. Report on progress of investigations in 1919. ALFRED H. BROOKS, *et al.* U. S. Geol. Survey, *Bull.* **714**, 237 pp.(1921).—This volume is the 16th of a series of annual bulletins treating of the mining industry of Alaska. An administrative report and 10 papers (representing 7 authors) on various features of Alaskan mineral resources are given. L. W. RIGGS

Gold deposits in the province of Pataz, Peru. A. GORDON PLEWS. *Bull. Inst. Mining Met.* 1921 (No. 202) 9 pp.—These deposits lie between 7 and 8° S lat. and about 77.5° W of Greenwich. Questions of access, transportation, power, climate and people are discussed. Au has been mined in this locality by primitive wasteful methods ever since, and probably before, the Spanish Conquest. The ores reported assayed from 0.65 to 7.46 oz. of Au and 0.39 to 5.37 oz. of Ag per ton with smaller amts. of As, Sb and Cu. L. W. RIGGS

Replacement copper deposits in the Warren district. GRAHAM JOHN MITCHELL. *Eng. Mining J.* **112**, 246–50(1921); cf. *C. A.* **14**, 1948.—This study of the Warren district, Bisbee, Ariz. is largely petrographic. "The outstanding geological features which have a bearing on prospecting for and developing ore may be summarized as follows:" Intimate association of ore with faults and fractures, which, together with bedding planes, have served to conduct mineralizing solns. to places of deposition. Close association of ore with granite-porphyry and quartz-porphyry intrusions. Occurrence of "knots" or bunches of chalcopyrite, bornite and chalcocite in low-grade pyrite, the presence of which may not be evident in a single opening in such material. This necessitates crosscutting and raising to prospect mineral bodies of this character. The importance of sooty chalcocite in enriching pyritic replacements. This enrichment is not always evident, and such material should be thoroughly prospected. The presence of enriched pyritic masses below leached siliceous breccia especially when such masses are strongly fractured and broken by faulting. Displacement of ore by post-mineral faulting. Many large ore bodies have been thus affected. Occurrence of ore in Paleozoic formations and Sacramento Hill porphyry. L. W. RIGGS

Deposits of manganese ore in Montana, Utah, Oregon, and Washington. J. T. PARDEE. U. S. Geol. Survey, *Bull.* **725-C**, 141–243(1921).—In 1917 the yield of

Mn ore in the Philipsburg district so greatly increased as to place Montana far ahead of other states in Mn production. The estd. reserve in the state is placed at 250,000 tons of high-grade ore, with a strong probability of a discovery of large additional deposits. Twenty-one mines and prospects in the Philipsburg district are described. In the Butte district the deposits have the advantage of being easily mined. There are several other deposits within the state. In Utah, from 1901–1918 about 16,000 tons of Mn ore were mined, three-fourths of it during the war. Reserves in sight are placed at 31,000 tons. Twenty-two mines and prospects are described. Somewhat less than 1000 tons of Mn was mined in Oregon in 1917–1918. The mines and prospects described number 14. About 500 tons of Mn ore were mined in Washington prior to the end of 1918. Despite the small production the deposits in this state give indications of future profit. Much of the ore consists of *bementite* of the compn. SiO_2 39.92, Al_2O_3 1.32, FeO 4.15, MnO 41.58, MgO 4.46, CaO 0.40, H_2O below 100 0.49, H_2O above 100 7.90, sum 100.22%. Several mines and prospects are described. L. W. RIGGS

Deposits of chromite in California, Oregon, Washington and Montana. J. S. DILLER, L. G. WESTGATE AND J. T. PARDEE. U. S. Geol. Survey, *Bull.* **725-A**, 1–84 (1921).—These 4 papers give the distribution and petrographic relations of the chromite-bearing minerals in the states mentioned. The genesis of the ores is discussed at length by D. The U. S. has reserve deposits adequate to supply a war demand for several years. Since the war this country is conserving its domestic supplies by employing high-grade and cheaper ores from foreign countries. L. W. RIGGS

Contact-metamorphic tungsten deposits of the U. S. FRANK L. HESS AND ESPER S. LARSEN. U. S. Geol. Survey, *Bull.* **725D**, 245–309(1921).—Of the 5061 tons of concentrates carrying 60% of WO_3 produced in the U. S. in 1918, 2734 tons were of scheelite and of this scheelite 1427 tons were from contact-metamorphic deposits. These latter W. deposits "have been formed through the combined action of the heat and solns. emanating from a cooling intrusive granitic magma on limestones and other intruded rocks and to a less extent on the granitic rock itself, by which the rocks are altered to or replaced by an aggregate of garnet, epidote, diopside, quartz, calcite, scheelite and other minerals." The W mineral of such deposits is invariably scheelite. The principal deposits are in the Great Basin region of Cal. and Nevada. The ore has also been found in Utah, Oregon, Ariz., N. Mexico and Alaska. Deposits of 25 districts, embracing a much larger number of claims and prospects, are described. L. W. R.

Geology of the Cement Oil Field, Caddo County, Oklahoma. FRANK REEVES. U. S. Geol. Survey, *Bull.* **726B**, 41–85(1921).—Caddo Co. is in the southwestern part of Okla. From 1916 to March 1920, 26 wells were drilled, 20 furnishing oil, 4 gas, and 2 were abandoned. At the latter date 36 wells were being drilled. Oil is found in a series of shales and sandstones at a depth ranging from 1500 to 2400 ft. The 20 wells furnish approx. 1200 barrels a day. The rate of decrease from initial production averages 2% a month, indicating that the wells will have a life of 6 to 8 years. The oil is fairly uniform, black, sp. gr. 0.84 to 0.85, and 35 to 40% of the oil distils below 250°. L. W. RIGGS

Oil prospects in Washington County, Utah. HARVEY BASSLER AND JOHN B. REESIDE, JR. U. S. Geol. Survey, *Bull.* **726C**, 87–107(1921).—Washington is the extreme southwestern county of Utah. Oil was discovered in 1907 when a slight amt. of drilling was done and the work abandoned. In 1918 the work was resumed and by Sept. 1920 the total production from 4 uncased wells 550 to 600 ft. deep was about 20 barrels a day. The oil is reported to range in gravity from 25 to 35° Bé., to have a paraffin base that includes some asphalt, and to contain S. It is dark brown and very fluid. The value of this region as a possible producer of oil is impossible to gage in advance of drilling. Suggestions for prospecting are given. L. W. RIGGS

Mineral resources of the United States in 1918. EDSON S. BASTIN AND MARTHA B. CLARK. U. S. Geol. Survey, *Mineral Resources of U. S., 1918,* Part I, 7a–145a (preprint B, published Aug. 15, 1921). E. H.

Preliminary note on monticellite alnoite from Isle Cadieux, Quebec. N. L. BOWEN. *J. Wash. Acad. Sci.* **11,** 278–81(1921).—The rock shows the two olivines chrysolite and monticellite, the latter usually in greater amt. The chrysolite, together with augite, occurs in early formed crystals, while the monticellite, as well as melilite and biotite, occur as ground mass minerals that have attacked and resorbed the chrysolite and augite. Chem. analysis by H. S. Washington gave: SiO_2 33.26, Al_2O_3 5.90, Fe_2O_3 5.30, FeO 6.54, MgO 26.41, CaO 14.47, Na_2O 1.23, K_2O 0.82, H_2O+ 1.91, H_2O- 0.09, CO_2 1.10, TiO_2 2.15, P_2O_5 0.76, MnO 0.15, Cr_2O_3 0.05, BaO 0.08, SO_3 0.22, sum 100.44%. Monticellite alnoite is a newly recognized but not a new rock, for some of the alnoite of the original type locality is found to hold monticellite showing the same relationships. L. W. RIGGS

Crystallization and resorption in the magma of the volcano Ruang (Sangi Islands). H. A. BROUWER. *Proc. Acad. Sci. Amsterdam* **23,** 561–9(1921).—Rocks from the eruptions of 1904 and 1914 both consist in the main of hypersthene augite andesite, but numerous xenoliths contain olivine and amphibole, characterized by more or less complete resorption. It is assumed "that the magma beneath Ruang was in its upper parts, before the commencement of the eruption, under pressure and temp. relations in which first pyroxene and later on at a subsequent cooling amphibole could crystallize, while at greater depths the field of crystn. of the amphibole was not reached." On effusion the lower lying more liquid lava crystd. as a hypersthene augite andesite, containing the fragments of its previously partly crystd. crust as xenoliths. G. W. MOREY

Deposits of mixed sulfide minerals in Sardinia (SANNA) **9.**

9—METALLURGY AND METALLOGRAPHY

D. J. DEMOREST, ROBERT S. WILLIAMS

The role of acid and slimes in flotation. B. H. MCLEOD. *Eng. Mining J.* **112,** 213(1921).—A sample of concentrates was taken from the head of a pneumatic machine which was treating a feed running 3% Cu, the minerals being chiefly chalcopyrite and pyrite. These concentrates were recleaned and freed from slime and could not again be floated without the addition of acid or slimes. It appears that after removing the slimes, the oil will not flocculate the larger particles of mineral but on the addition of acid or slimes the minerals are immediately flocculated. R. S. DEAN

Flotation of pyrite. WALTER S. MORLEY. *Trans. Am. Inst. Mining Met. Eng.* **1921,** No. 1085-M, 17 pp.—A series of tests made on sulfide minerals from 3 different localities is described. Of 22 standard oils and oil mixts., only 4, Pentarco Nos. 350 and 400, acid sludge and a mixt. of coal-tar creosote, wood creosote and coal tar, gave recoveries above 90% when tested on ore from the Mountain Copper Co. By considering both concns. and recovery the mixt. gave the best results. Four of the flotative agents used, G.N.S. No. 20, G.N.S. No 28, kerosene and crude oil, had no action under the conditions of the tests. The recovery of Zn as sphalerite is generally higher than that of either pyrite or chalcopyrite. The recovery of Cu as chalcopyrite is variable; the highest recovery (93.2%) was obtained by the use of X cake and xylidine in alk. soln. This reagent at the same time gave much lower recoveries for both pyrite (47.9%) and Zn (71.0%), thus indicating possibilities of selective flotation. H_2SO_4 was by far the most effecient of the modifying agents used. The increase in concn. of pyrite is particularly noticeable. Sodium silicate was somewhat effective in causing a selective

flotation of the Cu. NaOH and Na_2S gave, in most cases, a distinct sepn. of sphalerite from chalcopyrite, *i. e.*, a high Cu and low Zn, by suppressing the flotation of the sphalerite. Tarnish tended to prevent flotation. The action of the flotative agents on the other ores tried was very similar to that on ore from the Mountain Copper Co. The finer the material the greater is the percentage of recovery; the pyrite should pass at least a 170-mesh screen in order to get efficient flotation under the conditions of the tests. R. S. DEAN

Separation of sphalerite, silica and calcite from fluorspar. JOHN GROSS. Bur. of Mines, *Repts. of Investigations* No. **2264**, 3 pp.(1921).—The ore tested contained 7.3% Pb, 27.9% Zn, 35.7% CaF_2, 9.5% SiO_2 and 4.7% calcite. A comparison between electrostatic sepn. and flotation results leads to the conclusion that flotation will yield a slightly higher grade Zn concentrate with a much higher recovery, but that a marketable spar can be obtained in the tailing products of the flotation only by sacrificing a large amt. with the silica and calcite discarded on the tables. Practically any grade of spar can be obtained electrostatically. R. S. DEAN

Deposits of mixed sulfide minerals in Sardinia. EDOARDO SANNA. *Rass. min.* **54**, 102–3(1921).—Certain sulfide ores contg. Pb, Cu, Zn, Fe and Ag can be treated more advantageously with HCl, with partial conversion into chlorides, than by flotation and other mechanical means. M. R. SCHMIDT

Losses in the smelting industry. VICTOR TAFEL. *Metall u. Erz.* **18**, 377(1921).—Losses in smelters can be divided into the following groups: (1) Losses in waste material, this includes slag losses, losses due to absorption by muffles and crucibles, and metal contents in residues and waste liquors. (2) Vaporization and dust losses. (3) Loss in market products, as for example the noble metal content of hard and soft lead. The losses falling under 1 and 3 cannot be appreciably lessened. Those under 2 can be practically eliminated by the installation of suitable condensation app. Losses in slags and waste materials can be easily calcd. from the wt. of the material and the analysis, as is also true of losses in market products. It is practically impossible to evaluate accurately the vapor and dust losses. R. S. DEAN

Gold, silver, copper, lead and zinc in Nevada in 1919. Mines Rept. V. C. HEIKES. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Pt. I, pp. 373–416(preprint No. 17, published Aug. 16, 1921). E. J. C.

Gold, silver, copper, lead, and zinc in Montana in 1919. Mines report. C. N. GERRY. U. S. Geol. Survey, *Mineral Resources of U. S., 1919*, Pt. I, pp. 497–535 (preprint No. 20, published Aug. 17, 1921). E. J. C.

Advance statement of the production of copper in the United States in 1920. H. A. C. JENISON. U. S. Geool. Survey, Pamphlet, 7 pp.(1921). E. J. C.

Nevada Consolidated Copper Company. IV. Concentration of the ore. ARTHUR B. PARSONS. *Mining Sci. Press* **123**, 323–31(1921); cf. *C. A.* **15**, 3266.—A detailed, illustrated description of concn. operations with flow sheets showing the progress of metallurgical improvements. The use of ¼ lb. of a mixt. of 60% of α-naphthylamine and 40% xylidine per ton of ore as a flotation reagent has made it possible successfully to float the so called "rusty" chalcocite ore. An alternative combination of thiocarbanilide with *o*-toluidine and aldol or "fizzol" may also be used. The reagent is used in combination with an alkali which ppts. ferric salts, which would otherwise interfere with the xylidine mixt. The flotation app. is of the pneumatic type, as mechanical agitation offers no advantages and is more costly. A. H. HELLER

Operations of British America Nickel Smelter and Refinery. ANON. *Can. Chem. Met.* **5**, 229–30(1921). E. J. C.

Detroit Steel Casting Company plant. H. M. LANE. *Blast Furnace and Steel Plant* **9**, 522–4(1921).—An illustrated description. E. J. C.

Blast furnace gas poisoning. OTTO JOHANNSEN. *Stahl u. Eisen* **41,** 1141(1921).—The dulling of the mental faculties observed in several cases of severe blast furnace gas poisoning has nothing to do with the purity or kind of purification of the gas. This phenomenon is not caused by an unknown poison but is a typical symptom of CO poisoning. Although pure gas is just as dangerous as crude gas and blast furnace gas is being more and more widely used, no increase in gas poisoning is to be feared because of better arrangements for its use. R. S. DEAN

Blast furnace charging devices. A symposium of the Verein deutschen Eisenhuttenleute. I. Rhenish steel works of Duisburg Meiderich. H. LENT. *Stahl. u. Eisen* **41,** 945-54(1921). **II. Bochum Company of Bochum.** P. JAEGER. *Ibid* 994-99. **III. Gelsenkirchener Bergwerks-Akt.-Ges. blast furnaces, Gelsenkirchen.** E. OPDERBECK. *Ibid* 1064-71.—A detailed description of the machinery for charging blast furnaces in use at the various plants. R. S. DEAN

The "Husson" stationary incline charging system for the blast furnace. H. BARRAL. *Rev. metal.* **18,** 92-5(1921).—By placing the large counterpoise slightly higher in the framework of the system a lighter car and bin, a less powerful motor, and consequently a lighter framework are required. The car is provided with a special counterpoise which enables the bin to be lowered considerably before dumping, thus eliminating the ore chute and permitting a greater height of the furnace and also a greater tonnage without overloading the framework. Diagrams and photographs are given. W. A. MUDGE

The use of powdered coal firing in iron smelters. G. BULLE. *Stahl u. Eisen* **41,** 985-94(1921).—Powdered coal firing has the following advantages: (1) complete combustion, (2) mechanical handling, (3) complete control, (4) use of inferior grade of coal and (5) simplicity of furnace construction. The disadvantages are: (1) high first cost, (2) ash disposal, (3) a small storage capacity. R. S. DEAN

The heat ng of open-hearth furnaces with a mixture of brown coal briquet gas and blast-furnace gas. FRITZ BOETTCHER. *Stahl. u. Fisen.* **41,** 1027-30.—It has been shown that a mixt. of brown coal briquet gas and blast-furnace gas is very good for heating open-hearth furnaces if the proportion is correct. The gas producer must run slowly and at low temp. so as to evolve considerable tar vapor. The furnace must use large amts. of gas with high velocity. R. S. DEAN

Improvement in oper-hearth details. A. G. SCHUMANN AND A. F. SCHUMANN. *Iron Age* **108,** 269-72(1921).—An explanation of a new automatic reversing device developed by the authors, which has been applied to four 200-ton tilting furnaces at the Sparrows Point, Md., plant of the Bethlehem Steel Co. These new valves are of the mushroom type and the arrangement is such that it is possible to take the valve and seat out for repairs without delaying the operation of the furnace. The app. is operated by clock work reversing every 15 or 20 min. automatically. Sketches and operating diagrams are shown, also the arrangement on the furnaces. E. G. JARVIS

The preparation of the dolomite-tar mixture in Thomas (basic converter) steel works. MAX BACKHEUER. *Stahl u. Eisen* **41,** 954(1921).—The chem. and phys. properties of the dolomite have an important bearing on the life of the converter lining. Burnt dolomite with slight loss on ignition is best but the dolomite should not be sintered since this prevents the absorption of the tar. The mixt. for the converter walls should contain 35-40% powder, 30% fine and 30% coarse dolomite mixed with 8-10% of tar. The converter bottoms are made from a mixt. of 45-50% powder, 25% fine and 25% coarse dolomite with about 12% tar. R. S. DEAN

Cupola operations. FRITZ BRAUN AND GEORG HOLLENDER. *Stahl u. Eisen* **41,** 1021-27(1921).—Expts. were made on 2 cupolas to det. the completeness of combustion. The analysis of throat gases showed an av. of 17.14% CO_2, 2.77% CO, 0.44% O

and 79.65% N_2. The temp. of the Fe was 1275–1375° and the throat gas temp. 75–500°. The CO_2 content varied with the coke bed and the blast; the max. possible CO_2 is 19.05%. A theoretical calcn. from the C, H and S content of the coke gives 20.05%. A heat balance shows a 27.5% heat loss in radiation. The thermal efficiency of the cupola is directly proportional to the time of operation and the radiation loss proportional to the ratio CO_2 : CO. The thermal efficiency of the 2 furnaces expressed as η, heat content of the iron ÷ heat of combustion of coke and iron, was $\eta = 9.398$ for one furnace and $\eta = 0.447$ for the other furnace. R. S. DEAN

Continuous foundry for pipe fittings. HENRY M. LANE. *Iron Age* **108,** 519–24 (1921); illus. E. J. C.

Anti-friction bearings in the steel mill. A. M. MACCUTCHEON. *Assoc. Iron Steel Elec. Eng.* **3,** 321–50(1921). E. J. C.

Metal spray machines. N. MEURER. *Metall u. Erz* **18,** 384(1921); cf. *C. A.* **15,** 2049, 3266.—A description of the Meurer-Hopfelt metal spray machine. The machine is built like a sand-blast machine, the parts to be metal-coated being sand blasted first to clean them. It can be used for coating articles with Zn, Pb, Al, brass, Cu or bronze. The metal is sprayed in with a pistol of the Schoop type. The trommel of the machine is held at an elevated temp.; the nearer it approaches the m. p. of the metal coating the better the process works. The duration of the process for the Zn coating is 8–10 min. at 80–100°. The layer of Zn is $^1/_{10}$–$^1/_{30}$ mm. thick. For Pb the process lasts ½ hour, as thicker coatings are required. For Al, brass and bronze coating 50–75 min. are required and a temp. of 150–200°. If it is desired to follow the process with a polishing operation the time should be doubled. R. S. DEAN

Colloidal state in metals and alloys. JEROME ALEXANDER. *Mining Met.* **1921,** No. 169; *Tech. Paper* No. **1038,** 32–9; cf. *C. A.* **15,** 47.—Discussion of the orginal paper by P. D. Mercia, E. E. Thum, Zay Jeffries, P. W. Bridgman, H. Le Chatelier, and C. Benedicks. Among the facts brought out in discussion are the following: It is old furnace practise to est. the C in steel from the grain length of a quenched button. Flakes or woody structure in Ni steels are obviated by small amts. of alloying elements which flocculate the trouble-making impurities. The effects of subdivision extend above the colloidal zone. When water is frozen under high pressures, there is evidence of a mol. aggregation that persists in the liquid water. With fine dispersions the surface energy (=surface tension × surface) becomes enormous. Fe-Ni alloys form colloidal systems. In reply Alexander epitomizes 12 items omitted in the condensation of his paper. Answering Le Chatelier's criticism that no account was taken of surface tension, A. points out that he has gone beyond surface tension, to the forces that produce it. Benedicks believes that troostite represents the inferior limit of colloidal dispersion of cementite, with martensite as a solid soln.; whereas A. considers martensite and hardenite colloidal. The influence of metals on each other's crystallization is shown by comparing the aborted crystallization of a composite Pb-Sn tree with Pb and Sn trees separately formed. JEROME ALEXANDER

Season cracking of brass and other copper alloys. H. MOORE, S. BECKINSALE AND CLARICE E. MALLINSON. *Engineering* **112,** 262–4, 297–9, 327–30(1921).—See *C. A.* **15,** 1685. E. J. C.

New investigations of nickel brasses. L. GUILLET. *Rev. metal.* **17,** 484–95 (1920); *Chem. Met. Eng.* **24,** 261–5(1921); *Iron Age* **107,** 1380(1921).—Low-Cu brasses contg. 0.50%–27.76% Ni were studied. Above 10% Ni the alloys are not commercially important; below 10% alloys were found to give an ultimate strength of 90000 lbs. per sq. in., an elongation of 20%, and a resiliency of 8–10 kg. They show interesting variations in color from a white (12.87% Ni and greater) to a golden yellow (4.17% Ni), and in addition are quite resistant to atm. corrosion. The coeff. of equivalence varies

from −1.1 to −1.4; the same value for CO brasses is −0.1 to −1.5. Brass contg. a little Ni permits easier cold working; with $\alpha+\beta$ brasses contg. nearly all α (68:32), Ni supresses the β and makes hot working very difficult and sometimes impossible. Cu − 54, Zn − 41, and Ni − 5 is the best alloy; the 49:41:10 alloy is second best. Brasses with very high Ni content exhibit good $\alpha+\beta$ microstructures but have no specially valuable properties. The low-Ni brasses are not difficult to machine altho they are not as easy as ordinary brass. A small amt. of Pb facilitates machining. Alloys of 45% Cu, 45% Zn and 10% Ni contg. 1, 2, 3, and 4% of Pb in place of the Zn were studied. Up to 3%, Pb has no harmful effect at ordinary temps. on the mechanical properties of the alloys; at higher temps. the effect of Pb is more marked. Hardness decreases rapidly with increased temp., reaching about 50 at 500°; the resiliency increases from 2–9 kg. at 700–800°. Ni is destined to play as important a role in the brasses as it does in steel. Photomicrographs are given. W. A. MUDGE

Monel metal has definite magnetic properties. C. W. BURROWS. *Elec. World* **78,** 115–6(1921).—This Ni-Cu alloy has been found to have definite magnetic characteristics, its permeability being somewhat lower than that of Ni. Its critical point is only about 95°, hence it should have important uses such as in relays for temp. control equipment. Magnetization curves for several samples of the com. alloy (analyses given) in the form of bars, rods and sheets are shown. The permeameter and method used in the magnetic examn. are described. Hot-working of monel increases its magnetic softness. C. C. VAN VOORHIS

The ternary aluminium alloys. M. WAEHLERT. *Metall u. Erz* **18,** 298(1921).—The casting properties, structure, sp. wt. and physical properties have been detd. near the Al end of the ternary series Cu-Zn-Al, Fe-Zn-Al, Cu-Sn-Al. The investigations covered alloys up to 12% of the heavy metal. R. S. DEAN

The influence of cerium on the properties of aluminium and its important light alloys. JOSEF SCHULTE. *Metall u. Erz* **18,** 236(1921).—With pure Al and with alloys of Al and 3% Cu and of Al and 3.3% Mg small Ce additions increase the elongation without affecting the tensile strength. With an alloy of Al with 4% Ni and with Electron metal there is no difference. Al alloys with 25% Zn and Cu alloys with 10% Al, as well as pure Cu, show negative results. It has been shown analytically that the action of the Ce is due to the removal of the N in combination with the Al. R. S. D.

Determination of the quality and characteristics of steel and non-ferrous metals. TINIUS OLSON. *Raw Material* **4,** 169–79(1921).—Description and photographs of various types of machines used in the testing of steels and non-ferrous metals and alloys, together with a discussion of some of the methods used. H. C. PARISH

Molybdenum and molybdenum steel. ARTHUR H. HUNTER. *Blast Furnace and Steel Plant* **9,** 426–9(1921).—The manuf., properties and uses of Mo steel are discussed at length, together with a section on heat treatment, forging and cold pressing. Comparing Mo steels with other alloy steels, which are in the same category from a com. standpoint and treated similarly, shows for Mo steels: "(1) A higher elastic limit, hence a somewhat higher elastic ratio; (2) a higher elongation, hence greater ductility; (3) a much higher reduction in area, hence appreciably greater toughness." Emphasis is also laid on the possibility of a wide heat range in treatment of Mo steels. E. G. J.

The thermic analysis of a steel. EMILIO JIMENO. *Anales soc. espaÑ. fis. quim.* **18,** 165–73(1920).—A sample of steel (C, 0.44%; Mn, 0.36%) was heated to 1112° and allowed to cool slowly. Sixteen hrs. were required to reach room temp. By means of a thermocouple in contact with the specimen the temp. was noted at suitable intervals and the cooling curve plotted. The curve did not differ materially from one obtained by heating the same sample to 900° and allowing it to cool quickly. L. E. G.

The metallurgy of high-speed steel. D. M. GILTINAN. *Trans. Am. Soc. Steel*

Treating **1**, 716–26(1921).—A review of the production of high-speed steels during the past 50 years with analytical, heat treatment, and photomicrographical data which show typical compn., properties and structures. The theories of self-hardening are briefly discussed. W. A. MUDGE

Heat treatment of high-speed steel. J. L. THORNE. *Trans. Am. Soc. Steel Treating* **1**, 727–32(1921).—The best procedure is to heat to 2375° F. or slightly higher in a non-oxidizing atm., remove quickly when a thin section shows a faint but noticeable intensity of color, similar to recalescence of plain C steels, and quench in a salt bath at 1110–1130° F. When the steel has reached this temp., it is removed from the bath and allowed to cool to some point below 650° F., and then drawn at 1130–1175° F. Quenching in the molten salt bath eliminates the difficulties of cracking in the oil baths. The effects of different alloying elements are briefly reviewed. W. A. MUDGE

Volume changes in the heat treatment of steel. LESLIE AITCHISON. *Trans. Am. Soc. Steel Treating* **1**, 734–7(1921).—A discussion of cracks produced on quenching steels from the viewpoint of the "mass effect," which causes stresses to be set up in the exterior layer owing to a difference in the rate of cooling. Precautions should be taken to avoid a concn. or accentuation of this stress by the condition of the surface of the steel. W. A. MUDGE

Observations made in the heat treatment of ordnance forgings. PAUL E. MCKINNEY. *Trans. Am. Soc. steel Treating* **1**, 738–45 (1921).—Charts are given to illustrate how complete data of the melting operations may assist in the heat treatment and production of highest grade forgings. W. A. MUDGE

The carbonizing process. Relation of temperature to quality of case and core. THEODORE G. SELLECK. *Trans. Am. Soc. Steel Treating* **1**, 655–66(1921); cf. *C. A.* **15**, 2615.—The second of a series of 10 articles. The relation of temp. to quality of case and core for C steels is linear between the following points: 2012° F.: 2.50% C, and 1292° F.: 0.50% C. Quenching direct from the pot may result in very serious losses. The heat treatment after carbonization must be governed by the future service of the product. A single quenching for carbonized parts should always be avoided where it is economically possible and should never be chanced where the carbonizing temp. exceeds 1650° F. Surface cracks are due to improper temp., improper carburizers, and poor use of good carburizers. Cases are cited where an excessive temp. was established in carbonizing boxes and increased there, after the temp. of the furnace has been lowered, owing to very combustible carburizers made chiefly from coal products containing oil and other hydrocarbons which produce gas at very low temps. and at such velocity that the sealing box was of no use. An imperfect box will cause the same result. W. A. MUDGE

The delayed solution and premature precipitation of cementite in steels and the effect of the initial condition of the metal on this phenomenon. A. PORTEVIN AND P. CHEVENARD. *Compt. rend.* **172**, 1490–3(1921).—Heating and quenching a steel gives rise to 2 reactions: (1) soln. of Fe_3C in γ Fe, and (2) retention of this soln. at ordinary temps. If the original heating before quenching were insufficient to give a thoroughly homogeneous austenitic structure, a premature pptn. of cementite results owing to the formation of a nonuniform martensitic-carbon mixt. Differential dilatation curves for eutectoid carbon steels show a period of strong dilatation just before A_r, similar to that observed with hypereutectoid steels. The steel in this A_r region is actually locally hypereutectoid, the C content is greater than 0.90%, and a premature pptn. of Fe_3C occurs. This phenomenon, supplementary to the heating operation, is called the "delayed solution of the cementite." The rate of (1) depends largely upon the original condition of the metal. W. A. MUDGE

Effect of heat treatment on the fatigue strength of steel. E. P. STENGER AND B.

H. STENGER. *Trans. Am. Soc. Steel Treating* **1**, 617–35(1921).—C spring steel contg. 1.03% C, 0.45% Mn, 0.025% S, and 0.026% P was used. Bars of steel 18″ long, 2″ wide, and 9/32″ thick were quenched in oil at 100° F. from temps. of 1300° to 1700° F. The test bars quenched at each of these temps. were drawn at 450–1050° F. Both tension and fatigue tests were made for every combination of heat treatments, the av. of 3 tests being used to establish all values. The heat treatment was carried out in an elec. muffle furnace in which the temp. was brought up quickly to that desired for quenching; the total time in the furnace was about 50 min.; the quenching temp. was held for 15 min. For fatigue strength a vibratory machine was used in which the nominal unit stress as calcd. by the deflection formula fluctuated from 0–150,000 lbs. per sq. in., at the rate of 550 times per. min. The test piece acted as a cantilever beam, one end being clamped tightly while the load was applied at the other end thus causing deflection in one direction only. The drawing temp. does not affect the fatigue strength when the quenching temp. is below the Ac_1 point; when the quenching temp. is between Ac_1 and 1600° F. and the drawing temp. is below 500° F., the steel does not offer great resistance to fatigue, owing to internal stresses set up on hardening and the inability of the material to undergo deformation. There is one certain quenching temp., 1460–1480° F. which is just high enough to obliterate the previous existing grain structure, as well as one certain drawing temp., 600–700° F., which yield max. results. This quenching temp. corresponds closely to the Ac_{cm} point. These conclusions may not hold for alloy steels. Complete data are given in tables and curves together with a good review of previous work in this field. W. A. MUDGE

Influence of manganese on the mechanical properties of malleable castings. E. LEUENBERGER. *Stahl u. Eisen* **41**, 285–7(1921).—Expts. show that so far as mechanical properties are concerned more than 0.4% Mn is desirable. The following relations between Mn content, duration of annealing and mechanical properties have been found: (1) with increasing Mn content the tensile strength increases; (2) up to 1% Mn has no influence on the elongation; with higher percentages the elongation decreases; (3) tensile strength decreases with longer annealing and elongation increases; (4) the longer the annealing period the higher may be the Mn content without affecting the elongation adversely. R. S. DEAN

Investigations on the Baumann sulfur test and a contribution to the relations of phosphorus and iron. P. OBERHOFFER AND A. KNIPPING. *Stahl u. Eisen* **41**, 253–8 (1921).—Heyn's criticism of the Baumann sulfur print on the ground that P would also cause a blackening of the AgBr paper is unfounded. P does not interfere with the sulfur print. It is found that all the P is evolved from iron contg. P when treated with acid. The % evolved depends on the total present and the heat treatment. The following conclusions regarding the Fe–P system are drawn: (1) Pure Fe–P alloys become homogeneous by heating to 1200°. (2) The presence of C and other alloying elements makes the homogenizing more difficult. R. S. DEAN

Relative values of protective metallic coatings for iron and steel. S. O. COWPER-COLES. *Iron and Coal Trades Rev.* **103**, 102(1921); *Electrician* **87**, 50–1(1921).—There are 2 types of protective metallic coatings; electro-positive and electro-negative to the underlying iron or steel. The former includes Zn, Al and brass; the latter Pb, Sn, Cu and Ni, which are protective only as long as the coating remains intact, once penetrated, corrosion takes place more rapidly than before. Zn is most extensively used and can be applied in 4 ways: dipping in molten Zn, sheradizing, electro-zincing and spraying. The first process is the only one at present successfully employed for tank work and corrugated sheets. Its advantages are: its soldering action for making articles watertight; its rapidity; it ensures a considerable thickness of Zn except in the case of sheets or wire when it can be wiped off, leaving only a film. Its disadvantages: the coating

is not alloyed with the surface; it is economical only on a large scale and continuously; the waste of Zn is large; the flux, NH_4Cl, is expensive and helps to start corrosion; and paint does not adhere well. The spangled effect sometimes giving hot-galvanized sheets should be done away with. The advantages of sherardizing are: the Zn coating is evenly distributed, so that screwed or machined parts can be coated; the Zn alloys with the surface; the temp. employed is lower than with the molten process; the surface is excellent for painting; and the working costs are less and it can be worked intermittently. The disadvantages: There is no soldering action, hence vessels cannot be made tight; and a thin and inefficient coating will be applied if the temp. is too low. Electro-zincing has the advantages that it can be carried out in the cold, and large objects can be coated. Its disadvantages are: the Zn coating is uneven, building up on protruding parts, hollow parts receiving very little Zn; without careful supervision, the thickness of the Zn may be a mere film. The spraying process (cf. Schoop process, *C. A.* **13**, 2843; **14**, 3055) has the advantage that it can be applied to iron and steel structures when erected, but the process is very costly and the coating porous.

J. L. W.

Self-corrosion, not stray current electrolysis shown at Selkirk, Manitoba. W. NELSON SMITH AND J. W. SHIPLEY. *J. Am. Inst. Elec. Eng.* **40**, 642(1921). Preliminary note.—When the soil carries electrolytes in soln., self-corrosion is easily possible, in places where stray direct current electrolysis could not happen. A cast Fe water pipe, which had been imbedded in earth contg. salts, had been entirely free from access of stray d.c. and yet showed serious corrosion pits. Lab. tests are in progress on the effects of solns. of sulfates, chlorides and carbonates of Mg, Ca and Na (salts which are widely distributed through the soils of Western Canada). C. G. F.

The corrosion of iron and its prevention by the elimination of the gases dissolved in water. G. PARIS. *Chimie & industrie* **6**, 11–32(1921).—The various theories advanced to explain the corrosion of steam boilers are outlined and discussed, particular emphasis being laid on the presence of the dissolved gases and especially of O; and the various types of app. used for the elimination of these gases are described and their method of operation is briefly explained, special attention being paid to the Kestner-Paris app. for the removal of dissolved O and to its merits. A bibliography of French, British, American, German, and Swiss works on the subject is appended. A. P.-C.

Rusting experiments with iron containing copper. O. BAUER. *Stahl u. Eisen* **41**, 37–45, 76–83(1921); cf. *C. A.* **14**, 261.—Expts. were made with annealed and hot-rolled pieces and with unannealed pieces of iron under varying conditions. Conclusions: With hot-rolled test pieces (1) a definitely lower loss in wt. took place with Fe contg. Cu when subjected to industrial conditions. (2) With rusting in pure air the Cu is apparently without effect; this is also true of rusting in sea water and in the soil. With cast test pieces, unannealed, (1) small Cu additions do not affect the rusting in pure air or water. (2) The presence of Cu exerts a marked protective effect against water with high CO_2 content as well as against H_2SO_4. (3) P in Fe increases the rate of attack by H_2SO_4; the undesirable effect of P is neutralized by Cu. (4) Potential measurements in salt soln. contg. CO_2 show an increase in nobility on the addition of Cu to Fe.

R. S. DEAN

The preparation of slag for road ballast (SCHWARZE) (SCHÄFER) **20**. Polish for metals (U. S. pat. 1,381,250) **18**.

Recovering vanadium from ores. L. S. COPELIN. U. S. 1,381,802, June 14. V ore is heated with Na sulfide soln. in order to form Na vanadate. The reaction is carried out with steam under pressure.

The extraction of nickel from silicate ores. H. W. C. ANNABLE. Can. 183,827

Apr. 23, 1918. The silicate Ni ore is heated in a furnace in the presence of moist H_2S to convert the $NiSiO_3$ to NiS. A small amt. of NaCl may be added.

Reducing iron and lead ores. R. J. ANDERSON. U. S. 1,381,689 June 14. In the reduction of ores such as those of Fe and Pb, independent primary and secondary combustions are maintained, the primary combustion process comprizing the development of substantially complete combustion and the delivery of the combustion gases to the ore. The secondary combustion process comprizes the development of partially complete combustion, with an excess of C, and the products of the secondary combustion are delivered to the ore independently of those of the primary combustion so that the excess C is utilized for reduction of the ore.

Refining copper-nickel mat. N. V. HYBINETTE and R. L. PEEK. U. S. 1,382,361, June 21. Ni-Cu sulfate solns. such as are obtained from roasted mats and H_2SO_4 are brought into contact with an excess of finely divided Ni at a temp. of 40–60° in order to effect sepn. of Cu by cementation.

Basic open-hearth furnace. S. NAISMITH. Can. 212,542, July 19, 1921. A basic open-hearth furnace has a cooler positioned to serve as a neutral joint between the acid brick and basic lining to prevent fluxing. The furnace has brick stays adjacent its outer surface and an angle iron secured directly to the brick stays for supporting the furnace walls.

Furnace for heating metals. E. A. LESLIE and H. M. BRIGHAM. U. S. 1,382,002, June 21. The furnace is adapted for heating by gas flames.

Treatment of iron. C. B. TAYLOR. Can. 212,481, July 12, 1921. A mixt. of hematite, feldspar and an oxide of Mn and NaCl and a carrier consisting of oil-coated Fe turnings or borings is added to molten Fe in the process of making or in the foundry treatment. Increased malleability is claimed for the product of this process.

Tempering and refining iron or steel. F. VISINTAINER. U. S. 1,381,771, June 14. In tempering or refining Fe or steel the metal is coated with a "mineralized clay" comprizing SiO_2 61.12%, Fe_2O_3 7.92%, Al_2O_3 16.06%, CaO 6.39%, Mg 3.46%, S 0.86%, alkali 0.53% and moisture 3.66% mixed with H_2O to the consistency of a paste. The temp. of the coated metal is raised to the m. p. or lower and it is then shaped into the desired form.

Separating nickel from alloys. A. MCKECHNIE. U. S. 1,381,720, June 14. Cupro Ni alloy or scrap material contg. metallic Ni and Cu is melted and oxidized in a basic reverberatory furnace and the treatment is continued until all or part of the Ni is volatilized out or carried over from the furnace in the form of oxide which is collected and reduced to metallic Ni.

Degasifying and deoxidizing alloy. C. VOS. U. S. 1,382,146, June 21. An alloy adapted for use as a deoxidizing and degasifying agent in the production of ferrous metals is formed of Al 90–95, Mg 1.5–9.15, U 0.005–2.75, ferro-Si 0.5–1.25 and Fe 0.1–1.8 parts. U. S. 1,382,147 relates to an alloy adapted for the same purpose, formed of Al 90–95, Mg 2–10, ferro-Si 0.02–3.0 and Zr 0.01–6 parts. Cf. *C. A.* **15**, 499.

Hardening projectiles. R. A. HADFIELD, A. G. M. JACK and I. B. MILNE. U. S. 1,381,633, June 14. Ni chrome steel projectiles are heated all over to about 800–60° and then dipped, point downward to the base, in H_2O, and allowed to remain until hardened.

Magnet cores. J. W. HARRIS. U. S. 1,381,460, June 14. Magnet cores are formed by reducing electrolytic Fe, Ni or Co to the form of particles, annealing and flattening the particles, coating them with insulating material and molding them to the desired form under pressure.

Rust-proof piano wire, springs, tools, etc. M. J. UDY and F. C. NICHOLSON. U. S. 1,383,174, June 28. Piano wire is rust-proofed by electroplating it with a thin

coating of Cd, and then heating to a temp. of about 150–250° in contact with $Ca(OH)_2$ to effect alloying of the coating with the wire and superficial oxidation, and finally polishing the wire. U. S. 1,383,175 relates to a similar treatment of steel springs. U. S. 1,383,176 relates to rust-proofing edged steel tools or similar articles by a like method.

10—ORGANIC CHEMISTRY

CHAS. A. ROUILLER

Reduction of ethyl naphthoate. A case of the reduction of an alcohol to a hydrocarbon by sodium and absolute ethyl alcohol. HERVÉ DE POMMEREAU. *Compt. rend.* **172,** 1503–4(1921).—The reduction of α-$C_{10}H_7CO_2Et$ by Na and abs. EtOH gave, instead of the corresponding alc., a dihydromethylnaphthalene identical with that which is obtained by the similar reduction of α-$C_{10}H_7Me$. *The reduction of* α-$C_{10}H_7CH_2OH$ **(A)** *in similar manner gave the same hydrocarbon.* It was noted that **A** distd. with partial decompn. into the corresponding ether. O. B. H.

Oxalyl chloride. VI. The Friedel-Craft's reaction with oxalyl chloride. H. STAUDINGER, E. SCHLENKER AND H. GOLDSTEIN. *Helvetica Chim. Acta* **4,** 334–42(1921). —*α-Naphthol ethers.*—1-$C_{10}H_7OMe$ condensed with $(COCl)_2$ **(A)** in the Friedel-Crafts reaction gave ca. 60% yield of *1,1'-dimethoxy-4,4'-binaphthoyl* **(B)**, together with traces of an acid and small quantities of naphthol derivs. which were not investigated. No formation of the expected acenaphthenequinone deriv. was observed. **B** forms S-yellow crystals from glacial AcOH, m. 228–9°, and shows very little reactivity as compared with the acenaphthenequinone deriv.; it does not react with indoxyl and thioindoxyl as does Bz_2. Similarly, 1-$C_{10}H_7OEt$ gave *1,1'-diethoxy-4,4'-binaphthoyl* **(C)**, yellow-green leaflets from AcOH, m. 220–1°. *β-Naphthol ethers.*—When 1 mol. nerolin, (2-$C_{10}H_7OMe$) **(D)**, was condensed with 1 mol. **A** and 2 mols. of $AlCl_3$ in CS_2, the product consisted mainly, (ca. 50%) of *β-naphthofuran-1,2-dione* **(E)**. *1-Methoxyacenaphthenequinone* **(F)**, equiv. to 3–4% yield, was also isolated from the product by $NaHSO_3$ but the remainder of the residue was not studied further. Employing 1 mol. excess of **A** increased the yield of **E** very slightly while that of **F** remained very small. The use of large quantities of $AlCl_3$, (3 mols.) raised the yield of **E** to 53% but hindered entirely the formation of **F**. Changing the reaction mixt. to equiv. mol. proportions of **D**, **A** and $AlCl_3$ resulted in a 25% yield of **E** and traces of **F** but no 2-methoxynaphthoylformic acid, which it was hoped the change would produce, was obtained. Again, using 1 mol. of **A** and 2 mols. each of **D** and $AlCl_3$, only traces of **E** were formed while most of the product consisted of some neutral substance which was not investigated. **E** forms small, orange-yellow needles from hot AcOH or Me_2CO, m. 183° (decompn.), sol. in Na_2CO_3 and NaOH and is repptd. by acids, dissolves in warm alc. but is thereby changed, probably by partial esterification; similarly to benzofuran derivs., it reacts with $PhNHNH_2$ and o-$C_6H_4(NH_2)_2$. All attempts to prep. the MeO deriv. of **E** according to the methods of Rousset (*Bull. soc. chim.* **17,** 310(1897)) and of Graebe (*Ann.* **340,** 210(1905)) failed. 2-$C_{10}H_7OEt$ with 1 mol. **A** and 2 mols. $AlCl_3$ produced the corresponding *lactone, (1,1'-diethoxy-4,4'-binaphthoyl)*, in 6% yield together with traces of *1-ethoxyacenaphthenequinone.* The reaction with 2-$C_{10}H_7OCH_2Ph$ seemed to be very complicated; the product contained a new yellow *acid* which was not identified but neither lactone nor acenaphthenequinone formation was noted. With 2-$C_{10}H_7OPh$ a neutral, unidentified substance was the main product, traces of an acenaphthenequinone deriv. and an unknown acid also being present. *7-Methoxy-β-naphthofuran-1,2-dione* **(G)** was obtained in 45% yield, together with a small amt. of *2,7-dimethoxyacenaphthenequinone,* from the condensation of 2,7-$C_{10}H_6(OMe)_2$ **and A.** The use of a large excess of **A** did not improve the yield of either product. **G pptd. from** Na_2CO_3 is

a bright red powder which turns to brownish yellow when recrystd. from AcOH or PhMe; it m. 184° (decompn.) before recrystn., is insol. in Et_2O but dissolves in boiling alc. with alteration. Several attempts to prep. 1,8-$C_{10}H_6(OMe)_2$ desired for condensation were unsuccessful, having resulted in the formation of the mono-Me deriv. *Phenol ethers.*—*Anisil*, obtained in 80% yield from the condensation of anisole with **A** in CS_2, lemon-yellow crystals from alc., m. 133° (not 93° as given through error in *C. A.* **6**, 2617). *2,4,-2',4'-Tetramethoxybenzophenone*, from *m*-$C_6H_4(OMe)_2$ under identical conditions, pale-yellow crystals from alc. m. 129–30°. *2,5,2',5'-Tetramethoxybenzophenone*, from *p*-$C_6H_4(OMe)_2$, m. 109° (recrystd.). Veratrole gave *2,3,2',3'-tetramethoxybenzophenone*, m. 145°, and a small quantity of *veratril*, m. 214°. **VII. The Friedel-Crafts reaction with imido chloride derivatives of oxalic acid.** H. STAUDINGER, H. GOLDSTEIN AND E. SCHLENKER. *Ibid* 342–64.—The decompn. of $(COCl)_2$ by $AlCl_3$ into CO and $COCl_2$ renders it extremely difficult to prep. *o*-diketones by its use in the Friedel-Crafts reaction (see above). The authors carried out numerous expts. replacing the $(COCl)_2$ with imido chloride derivs. of $(CO_2H)_2$ in hopes of overcoming this difficulty. However, with the exception of the Me and Et ethers of 2-$C_{10}H_7OH$, which under the best conditions gave 75% and 44% yields, resp., of the corresponding acenaphthenequinone derivs., the results obtained with the imido chlorides were not very promising. Brown, amorphous decompn. products were formed in nearly all condensations tried and were frequently the sole products obtained. The same decompn. products appeared to be formed when the imido chlorides were allowed to react alone with $AlCl_3$ in CS_2 or C_6H_6. The condensations described below were generally carried out by bringing together equimol. amts. of the compd. under investigation and of the imido chloride with 2 mols. of $AlCl_3$ in CS_2 or C_6H_6, allowing the reaction to proceed a short time in the cold and then refluxing 2 hrs. After treating with 10% HCl, the solvent was steam-distd. and the reaction mixt. heated 0.5 hr. longer to break up the primary Schiff's bases. The product was then filtered off, washed and extd. with Na_2CO_3 for acidic compds. next warmed with aq. $NaHSO_3$ to isolate acenaphthenequinone derivs. and finally treated with NaOH to remove naphthol derivs. The remaining residue was examd. for cryst. compds., usually with negative results. *1. Naphthalene derivatives.*—$C_{10}H_8$ with PhN:CClCCl:NPh (**A**) formed principally a dark, amorphous decompn. product with traces of *acenaphthenequinone* (**E**), m. 225°. The reaction proceeded no better in the cold nor when anhydrous $FeCl_3$ was used in place of the $AlCl_3$. No definite compd. could be identified in the product of the condensation of 1-$C_{10}H_7OMe$ with **A**. The best yields (75–7% based on the amt. of **A** used), of the diketone from nerolin were obtained by adding with vigorous agitation a soln. of nerolin and **A** in C_6H_6 to $AlCl_3$ in the same solvent. Freshly prepd. $AlCl_3$ was found to be too reactive and gave poorer yields than the salt which had been prepd. for some time and contained a little H_2O. The use of different solvents (CS_2 and PhMe), a larger excess of $AlCl_3$ or a smaller quantity together with gaseous HCl, a longer period of heating (up to 48 hrs.), and the substitution of anhydrous $ZnCl_2$, $SnCl_4$ and $FeCl_3$ for the $AlCl_3$ were all tried but proved of no advantage with respect to the yield of the diketone. Neither were more favorable results obtainable by changing the order of mixing the reacting compds. *1-Methoxyacenaphthenequinone* (**C**), obtained from nerolin as just stated, crysts. from glacial AcOH in yellow leaflets, m. 215–6°, is almost insol. in alc., Et_2O and C_6H_6, sol. in concd. H_2SO_4 with deep red color and pptd. therefrom by dil. with H_2O. **C** suspended in boiling AcOH reacts with *o*-$C_6H_4(NH_2)_2$ in Et_2O, forming *11-methoxyacenaphthenequinoxaline*, bright yellow needles from alc., m. 182–3.5°. *β-Methoxyacenaphthene-indoleindigo* was prepd. according to the method employed by A. Bezdrick and P. Friedländer (*C. A.* **2**, 1438) for the analogous dyestuff from acenaphthenequinone, violet-black needles, sol. in AcOH, easily reduced and dyes cotton a bluish violet. *β-Methoxyace-*

naphthenethionaphtheneindigo, prepd. similarly from **C**, is an intensely red compd. (*methoxyciba scarlet*), sol. in concd. H_2SO_4 with deep blue color, somewhat more difficult to reduce than the unsubstituted dyestuff and imparts a deep red color to cotton. 2-$C_{10}H_7OEt$ gave a 44% yield of *1-ethoxyacenaphthenequinone* (**D**), m. 141–2°, more sol. than **C** in AcOH and other solvents. **D** condenses similarly to **C** with *o*-$C_6H_4(NH_2)_2$, indoxyl and thioindoxyl. Only traces of an acenaphthenequinone deriv. were obtained with 2-$C_{10}H_7OPh$ while 2-$C_{10}H_7OCH_2Ph$, 2-$C_{10}H_7OAc$ and 2-$C_{10}H_7OBz$ yielded none whatever. A 70% yield of *β-naphthofuran-1,2-dione* was obtained by the condensation of free 2-$C_{10}H_7OH$ with **A**. 2-$C_{10}H_7NMe_2$ could not be made to condense with **A** even when an excess of $AlCl_3$ was employed. 2-$C_{10}H_7NH_2$.BzOH formed only traces of a diketone deriv. The results were likewise negative with 2-$C_{10}H_7SMe$ and 2,6-$C_{10}H_6(OMe)_2$. When the condensation of 2,7-$C_{10}H_6(OMe)_2$ was carried out in the usual way, very poor yields of the diketone were obtained while some *7-methoxy-β-naphthofuran-1,2-dione*, m. 184°, also was formed. On the other hand, 24 hrs. heating in C_6H_6 as a solvent, led to the formation of an unidentified, red basic *dyestuff* similar to that observed with 2-$C_{10}H_7OMe$. Under the optimum conditions found for the condensation of the latter compd., a 51% yield of *1,6-dimethoxyacenaphthenequinone* (**E**) was realized. **E** is difficultly sol. in org. solvents excepting hot AcOH and $PhNO_2$. Recrystn. decomps. it easily, hence it is best purified through its $NaHSO_3$ soln. from which it is pptd. as an orange-red powder, m. 273°. **E** dissolves with deep blue color when warmed with dil. NaOH and $Na_2S_2O_4$ but is not regained unaltered on acidification; it unites with indoxyl and thioindoxyl in AcOH. *2. Diphenyloxalimidyl chloride with other aromatic compounds.*—No $NaHSO_3$-sol. product could be obtained by the condensation of acenaphthene, phenanthrene or Ph_2 with **A**. Attempts to condense anthracene with **A** under various conditions were made but not more than traces of the orange-red aceanthrenequinone, m. 266–8°, previously described by Liebermann and Zsuffa (*C. A.* **5**, 2251), could be isolated from any of the products. 2-$C_{14}H_9Me$ yielded small amts. of a new *aceanthrenequinone derivative*, m. 215–30°, which was probably composed of a mixt. of isomers. Unlike the corresponding naphthol deriv., 2-$C_{10}H_9OMe$ gave very poor yields of an *aceanthrenequinone derivative*, m. 210–20° (recrystd. from AcOH). *3. Benzene derivatives.*—Heating C_6H_6 or PhMe with $AlCl_3$ and **A** either for a short or long period resulted only in the usual dark decompn. masses; neither benzil nor tolil was observed. The same result was obtained by heating **A** in high boiling solvents with or without the addition of $AlCl_3$. Some *anisil*, m. 130°, was isolated from the red, resinous product formed by condensing anisole with **A**. *4. Other imido chlorides.*—*Di-o-tolyloxalimidyl chloride* when condensed with nerolin produced the corresponding *acenaphthenequinone derivative* in 62% yield. Attempts to condense it with C_6H_6 led to the same result as when **A** was tried. *Di-m-nitrophenyloxalimidyl chloride* (**F**), pale yellow crystals, m. 173°, sol. in C_6H_6 and PhMe, was prepd. by the action of PCl_5 on di-*m*-nitrophenyloxamide. Only a very small quantity of the acenaphthenequinone deriv. was formed in the condensation of nerolin with **F**. *Di-α-naphthyloxamide* (**G**), made by progressive heating up to 260° of 2 mols. of α-$C_{10}H_7NH_2$ with 1.1 mol. $(CO_2Me)_2$, is difficultly sol. in alc., m. 234°. Refluxing **G** for 6 hrs. with PCl_5 in C_6H_6 converts it to *di-α-naphthyloxalimidyl chloride* (**H**), golden yellow needles from C_6H_6 or Et_2O, m. 156–6.5°. **H** is strikingly stable toward H_2O and alc. but reverts back to **G** when heated with AcOH, HCl being split off; long heating in $PhNO_2$ decomps. it; by boiling it with $AlCl_3$ in C_6H_6, dark, amorphous masses are formed similar to the decompn. products obtained from **A**. In cold H_2SO_4, **H** dissolves with deep violet color; on heating the latter soln. HCl is evolved, the color changes to indigo-blue and then darkens through decompn. No formation of isatin as reported by Bauer (*C. A.* **1**, 2569; **3**, 2450) was observed. In contrast to **A**, **H** does not react with nerolin and $AlCl_3$ in CS_2.

Di-β-naphthyloxamide (I), m. 270°, was prepd. analogously to G, the yield being 87%. *Di-β-naphthyloxalimidyl chloride* (J), from I with PCl_5 in 93% yield, crysts. from C_6H_6 in pale yellow leaflets, m. 210–1° (decompn.), is less sol. than the α-isomer but shows a similar behavior toward H_2O, alc., AcOH, concd. H_2SO_4, etc. J did not react with nerolin in the Friedel-Crafts reaction. PhCCl:NPh gave no condensation product with C_6H_6. With anisole, however, an 89.5% yield of *β-methoxybenzophenone*, m. 60.5° from Et_2O, was obtained. Attempts to obtain an inner condensation product of 1-$C_{10}H_7$N:CClPh by refluxing it with $AlCl_3$ in C_6H_6, CS_2 and $PhNO_2$ proved fruitless. The corresponding amide, 1-$C_{10}H_7$NHCOPh, was regained in all cases. The results were analogous when 2-$C_{10}H_7$N:CClPh was tried. When dry $(CN)_2$ and HCl gases were passed into nerolin in cold CS_2 and $AlCl_3$ was added gradually, the product contained C equiv. to a 14% yield, the rest being a tarry neutral mass. The yield of C was slightly increased by carrying the reaction out at the temp. of the H_2O bath in a shorter time but dropped to 7% when 1 mol. of Cu_2Cl_2 was used in addition to the $AlCl_3$. A. T. F.

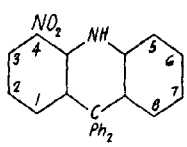
Tetrahydronaphthols. A. Brochet and R. Cornubert. *Compt. rend.* **172**, 1499–1500(1921).—Of the 4 possible tetrahydro-α- and β-naphthols, only 3 have previously been described. B. and C. have prepd. the 4th, *ac-tetrahydro-α-naphthol*, (A), by the hydrogenation of α-naphthol at 130° under 15 atm. pressure in the presence of 12.5% Ni. They obtained thus 85 parts of A and 15 parts of the aromatic deriv. (B). A b_{17} 139–140°, d_4^{17} 1.0896, n_D^{17} 1.5671. B m. 68°. The hydrogenation of β-naphthol gave similarly 25 parts of the aromatic deriv., m. 57.5°, and 75 parts of the aliphatic deriv. (C), b_{20} 144.5–6.5°, d_4^{17} 1.0715, n_D^{17} 1.5523. A gives a phenylurethan m. 121°, C gives one m. 99°. The hydrogenation by the method of Brochet (*C. A.* 3180) leads easily to the tetrahydronaphthols without formation of the decahydronaphthols. O. B. H.

Reduction of fluoreneoxalic ester. Wilhelm Wislicenus and Herbert Weitkmeyer. Univ. Tübingen. *Ber.* **54B**, 978–9(1921); cf. Sieglitz, *C. A.* **15**, 1316.—From 25 g. of the ester in 100 cc. Et_2O warmed under a reflux with Al-Hg with occasional additions of H_2O for about 12 hrs. until the yellow soln. has become colorless is obtained 15 g. *ethyl fluorenehydroxyacetate*, $(C_6H_4)_2CHCH(OH)CO_2Et$, felted needles from C_6H_6, m. 84°, 1.3 g. of which, boiled 1 hr. with the calcd. amt. of alc. NaOH, yields a small amt. of an almost colorless flocculent Na salt yielding on acidification a cryst. acid whose soln. is colored yellow by very dil. $FeCl_3$, indicating that this is probably the free *fluorenehydroxyacetic acid*. The main product of the reaction, however, remains in the alc. soln. which, when evapd., taken up in a little H_2O and acidified, yields *diphenyleneacrylic (dibenzofulvenecarboxylic) acid*, fine yellow needles from C_6H_6 or Et_2O, m. 222–3°, sol. in soda with pronounced loss of color. C. A. R.

The action of chloral oxime on the aromatic amines; synthesis of isatins. Th. Martinet and P. Coisset. *Compt. rend.* **172**, 1234–6(1921).—The reaction between CCl_3CH:NOH and aromatic amines may follow 2 different courses: (*a*) in a neutral medium 2 mols. of $PhNH_2$ may take part giving *diphenylisonitrosoacetamidine* (A), HON:CHC(:NPh)NHPh, (French pat. 291,359 (1899)) while, (*b*), in a slightly acid medium the product is *isonitrosoacetanilide*, PhNHCOCH:NOH (B) (French pat. 501-153 (1920)). When B is warmed with H_2SO_4 it forms *isatin*. The process requires but 24 hrs. and constitutes a very convenient method for the prepn. of ordinary isatin and other known isatins. A new isatin was prepd. according to the same method as follows: To 1 mol. of *p*-chloro-*o*-anisidine hydrochloride in 1.5 l. of H_2O, 1 mol. of $NH_2OH.HCl$ was added and the soln. brought to boiling; 1 mol. of $CCl_3CH(OH)_2$ in 1.3 l. H_2O was then added, in small portions at a time, and boiling maintained 5–10 min. longer. By cooling quickly, *2-methoxy-5-chloro-isonitrosoacetanilide*, HON:CHCONH-C_6H_3(OMe)Cl (C), sepd. out, m. 190°, sol. in alc. C gives a violet soln. in H_2SO_4 chang-

ing to reddish brown on warming. On heating **C** with 7 parts of concd. H_2SO_4 at 75° for 0.25 hr., cooling and adding an excess of H_2O, *4-chloro-7-methoxyisatin* (**D**) pptd. out. It was purified by dissolving in concd. Na_2CO_3, filtering and repptg. with HCl. **D** is insol. in H_2O, sol. in AcOH and boiling alc.; it is obtained from the latter as long, red needles, m. 255° on the Maquenne block. The *phenylhydrazone*, silky, yellow needles, m. 245°; the *oxime*, m. 230°, is sol. in alc. The *isatates* can be prepd. from **D** by the action of alc. solns. of the alkalies. *Barium isatate* was thus obtained, $C_9H_7O_4NCl$-$Ba.H_2O$, brown plates, sol. in H_2O, insol. in alc. The *copper isatate* was prepd. by double decompn. On condensing **D** with indoxyl, *4-chloro-7-methoxyindirubin* (**E**) resulted, violet needles, slightly sol. in alc. With hyposulfite **E** gave an unstable, greenish yellow vat which was soon transformed into ordinary indigo. A. T. FRASCATI

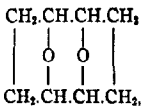
New synthesis of carbazine dyes. III. Colored derivatives of tetraphenylmethane. F. KEHRMANN, M. RAMM AND CH. SCHMAJEWSKI. *Helvetica Chim. Acta* **4**, 538–46 (1921).—K., R. and S. have attempted to carry out condensations similar to that effected by Turpin (*J. Chem. Soc.* **59**, 714(1891)), in going from *N*-picryl-*o*-aminophenol to 1,3-dinitrophenazoxine, for cases where the -OH is replaced by Me, CH_2R, and CHR_2, resp. Successful results were obtained in only a few special cases when both R's in the CHR_2 were aromatic. They have prepd. thus 4-nitrodiphenylcarbazine, dark red crystals, m. 210–7°, insol. in H_2O, but sol. in alc. and benzene, the alc. soln. giving no color change with alkali, and 2,4-dinitrodiphenylcarbazine, orange-yellow prismatic crystals, m. 232°, insol. in H_2O and cold alc., but sol. in hot alc. and very sol. in hot benzene, the alc. soln. turning deep red with alkali. This compd. has been reduced to the di-NH_2 compd. and then oxidized with $FeCl_3$ to *4-aminodiphenylcarbazimonium 2-chloride*, black shining needles, almost insol. in cold water but easily giving a brownish red hot soln. The earlier described isomers were olive-green to blue-green in color. By their synthesis of the two NO_2 derivs. above, the authors have verified the earlier surmizes as to the orientation of the NO_2 groups in the products obtained by the direct nitration of diphenylcarbazine. O. B. H.



Nitro derivatives of phenazonium. F. KEHRMANN AND JEAN EFFRONT. *Helvetica Chim. Acta* **4**, 517–26(1921).—K. and E. have shown that various NO_2 derivs. of phenazonium can be obtained by the oxidation with $FeCl_3$ or concd. HNO_3 of alkyl- or arylnitrodihydrophenazines (*Ber.* **26**, 2372). They have prepd. thus *N-methyl-1-nitrophenazonium perchlorate*, yellow crystals rather sol. in hot H_2O forming a fairly stable greenish yellow soln; *N-phenyl-1-nitro-phenazonium perchlorate*, a bright yellow cryst. powder whose hot H_2O soln. is citron-yellow and gradually decomps.; *N-methyl-1,3-dinitrophenazonium nitrate*, orange-yellow needles easily sol. in cold H_2O and easily reduced by skin, paper, or alc. to the violet hydrophenazine deriv.; *N-methyl-1,3-dinitrophenazonium perchlorate*, orange-yellow needles difficultly sol. in water, obtained in 90% yield from the dihydrophenazine deriv.; *N-ethyl-1,3-dinitrophenazonium perchlorate*, very similar to the Me deriv. and obtained in equal yield; *N-phenyl-1,3-dinitrophenazonium perchlorate*, reddish yellow crystals in 85% yield, almost insol. in H_2O; *N-phenyl-1,3,7-trinitrophenazonium perchlorate*, amber needles sol. in cold water with rapid decompn. The last deriv. explodes on gentle heating of the dry substance. K. and E. have also prepd. in similar fashion *N-phenyl-1-amino-3-nitrophenazonium perchlorate*, dark green crystals sol. in hot H_2O, but this deriv. probably exists in an imonium rather than an *azonium* form. O. B. H.

Condensation between formaldehyde and acetone. ARNO MÜLLER. Leipzig. *Ber.* **54B**, 1142–8(1921).—The HCH:CHAc which might be expected to result from the condensation of HCHO with Me_2CO has never been isolated. If alkali is used as the

condensing agent there is obtained either $AcCH_2CH_2OH$ or an amorphous substance (Werner, *Proc. Chem. Soc.* **20**, 196(1904); Elberfelder Farbenfabr., *Chem. Zentr.* **1919**, II, 347, 1421). In the present paper M. describes some observations on the latter substance (A) from which he concludes that it probably has the structure



resulting by loss of $2H_2O$ and rearrangement from 2 mols. of $AcCH_2CH_2OH$ first formed. A mixt. of 75 g. of 40% HCHO and 60 g. Me_2CO is rapidly poured into 50 cc. of 30% NaOH and 200 cc. of 96% alc., then after 36 hrs. into 2 l. H_2O, filtered and dried on clay; yield, 50–5 g. Various solvents were tried for the purification of the crude product but no characteristic crystals could ever be obtained; distn., even in a high vacuum, also led to deep-seated decompn. For the purification 50 g. of the crude product in 400 cc. hot alc. was treated with 100 cc. MeOH, cooled, filtered and dried on clay, the filtrate being similarly treated. It has no sharp m. p., carbonizes above 300°, has a faintly yellow-orange color and when dry is tasteless and odorless. When boiled with H_2O it evolves a hexenone-like odor. It is sol. in MeOH and EtOH, Me_2CO and C_6H_6, less in Et_2O, almost insol. in ligroin, H_2O and dil. alkali, quite sol. in AcOH, forms completely neutral alc. solns.; mol. wt. in freezing AcOH, 121.5. No phenylhydrazone nor oxime could be obtained by the usual methods. When 7 g. A and 40 g. KOH in 300 g. boiling H_2O is slowly treated with 32 g. $KMnO_4$, allowed to stand 1 hr. longer on the H_2O bath, treated with alc. to destroy the excess of $KMnO_4$, filtered hot and acidified with HCl, much CO_2 is evolved and the soln., on extn. with Et_2O, drying with Na_2SO_4 and evapg., gives a small amt. of a brown cryst. residue permeated with acids of a penetrating odor (AcOH, $EtCO_2H$, etc.), among which only AcOH was identified with certainty by the cacodyl reaction. From 5 g. A in 50 cc. boiling AcOH treated with 26 g. Br, and allowed to stand 24 hrs. is obtained 9 g. of a chocolate-brown odorless and tasteless powder, insol. in AcOH and H_2O, sol. only in traces in the usual org. solvents, insol. in KOH, evolves gas vigorously when heated with NH_4OH and H_2O_2 and has the compn. $C_3H_6O_2Br_2$; 5 g. heated 10 hrs. at 125–30° with about 30 g. quinoline yields 3.6–4.0 g. of an almost black, coal-like, tasteless and odorless substance with 11.78% Br, which again adds Br in H_2O. A (20 g.) allowed to stand 2 hrs. under 150 cc. HNO_3 and heated 6–7 hrs. at 100–10° until a red-brown soln. results which gives a yellow ppt. with H_2O, then freed from most of the free HNO_3 by evapn. *in vacuo*, taken up in H_2O and again treated in the same way twice, yields 11–2 g. of a *substance* $C_3H_6O_2(NO_2)_2$ which rubs to a light orange-brown odorless powder, forms in H_2O an intensely bitter soln. slightly acid to litmus, partially sol. in alkali with dark brown color, carbonizes on heating, slowly absorbs Br in AcOH, reacts at once with $KMnO_4$, mol. wt. in freezing H_2O, 224.5, m. 65–8°, decomps. 82–5°, forms with NaOEt in alc. a *sodium salt* as a voluminous ppt.; *iron salt*, from an alc. soln. treated with aq. neutral $FeCl_3$ and dild. with H_2O, voluminous ppt. CHAS. A. ROUILLER

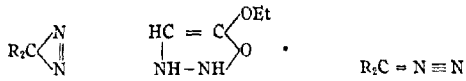
Aliphatic diazo compounds. XX. Reduction with hydrogen in the presence of palladium. H. STAUDINGER, ALICE GAULE AND J. SIEGWART. *Helvetica Chim. Acta* **4**, 212–17(1921).—The results of the authors' expts., like those of Darapsky (*C. A.* **6**, 2619; **12**, 900), harmonize better with the Angeli-Thiele than with the Curtius formula for the structure of aliphatic diazo compds. Diphenyldiazomethane, $Ph_2C{:}N{:}N$, in 60% alc. was reduced with colloidal Pd in the presence of H. The principal product was *diphenylmethane* (A), a small quantity of *benzophenone hydrazone* (B) also being formed. Neither NH_3 nor NH_2NH_2 was observed in the products; hence it is not likely that A

was produced by further reduction of the primary product **B.** Since the diazo compd. was found to react much more slowly with Pd alone than it did when H also was present, it seems improbable that a methylene deriv. was first formed by splitting off N and that **A** then resulted by the fixation of H on the methylene compd. The authors believe that the reaction is as follows: $Ph_2C{:}N{\cdot}\,N \xrightarrow{H} Ph_2CHN{:}NH \longrightarrow Ph_2CH_2 + N_2$ while a small part of the diazo compd. reacts directly to form the $Ph_2C{:}NNH_2$. The reaction appears analogous to the synthesis of hydrocarbons by the reduction of aromatic diazo compds. with alk. $SnCl_2$. The course of the reaction is different, however, when amalgams are used. Reduced in cold Et_2O with Al-Hg or Na-Hg, Ph_2CN_2 gave *diphenylmethylamine*, b_{12} 161–6°, but no **A.** The same result was obtained on reducing $Ph_2C{:}NNH_2$ with Al-Hg or Na-Hg. $(C_6H_4)_2CN_2$ in the presence of Pd, was reduced almost quant. to *fluorene*. The same product resulted by using Al-Hg as a reducing agent on $(C_6H_4)_2CN_2$ or fluorenone hydrazone in a large quantity of Et_2O. N_2CHCO_2Me and N_2CHCO_2Et in MeOH and EtOH, resp., yielded on reduction with colloidal Pd 65–75% of the corresponding *esters*. On the other hand, $N_2C(CO_2Et)_2$ on reduction with Pd did not furnish the ester but the corresponding *hydrazone*, $(EtO_2C)_2C{:}NNH_2$, m. 80° after recrystn. from C_6H_6 and petr. ether and identical with that prepd. from mesoxalic ester and $NH_2NH_2.H_2O$. **XXI. The constitution of hydrazones, especially of mesoxalic ester hydrazone.** H. Staudinger and L. Hammet. *Ibid* 217–28.— The reduction of diazomalonic ester by Paal's method yielded a hydrazine deriv. which S. and H. at first believed to be the *hydrazimalonic ester*, $(EtO_2C)_2C.NH.NH$ (**A**), and not

the *ketomalonic ester hydrazone*, $(EtO_2C)_2C{:}NNH_2$ (**B**). By a study of the properties of this hydrazine deriv. and comparison of its behavior with that of known hydrazones, the authors conclude that their first assumption was incorrect and that the compd. was a true *hydrazone* of formula **B.** In the course of this work a number of other hydrazine derivs. were prepd. and their behavior toward various reagents studied as noted below. **B** has been previously described by Neeresheimer (*Diss. München* **1908**); it was formed almost quant. by warming NH_2NH_2 with mesoxalic ester in very dil. AcOH and obtained as colorless crystals from C_6H_6-petr. ether, m. 80°, $b_{0.15}$ 100° without decompn. Refluxed with BzH in alc. for 1 day, benzalazine, m. 93°, was formed. Measurements of the f. p. depression in C_6H_6 indicated that **B** was associated in this solvent. This formation of double mols. would be difficult to explain were its structure that of **A.** When **B** was warmed with PhNCO on the H_2O bath, *ketomalonic ester phenylsemicarbazone* was formed, white crystals, m. 117°, from C_6H_6. $NH_2CONHNHPh$ did not react in H_2O with mesoxalic ester but reacted energetically with ketomalonic ester, yielding a *hydrate* of the *phenylsemicarbazone*, m. 126–8° (recrystd. from alc.); the latter did not lose H_2O even on heating *in vacuo* at 100°; refluxed in C_6H_6 soln. with P_2O_5 it was converted to the phenylsemicarbazone. Mesoxalic ester (5.8 g.), warmed on the H_2O bath with an aq. soln. of NH_2NMe_2 (1.8 g.) which had previously been neutralized with AcOH, gave the *dimethylhydrazone* of *ketomalonic ester* (**C**), viscous, pale-yellow oil, $b_{0.1}$ 106–8°. As would be expected from its formula, **C** showed no tendency to associate in C_6H_6. No change was produced when mesoxalic ester was added to hydrazimethane in AcOH; ketomalonic ester, in contrast, reacted very readily, yielding a viscous reaction product which $b_{0.15}$ 90–1° but was not sufficiently pure for analysis. $CO(CO_2Et)_2$ reacted immediately with NH_2NHBz, evolving heat and giving a product which m. 100°, recrystd. from C_6H_6, probably $(EtO_2C)_2C(OH)NHNHBz$. *Ketomalonic ester p-tolylhydrazone*, prepd., from mesoxalic ester and p-$MeC_6H_4NHNH_2$ in AcOH, pale, yellow-green crystals from ligroin, m. 77°. $PhCH{:}NNH_2$ reacted energetically with PhNCO in Et_2O giving the phenylsemicarbazone, m. 175°, identical with that prepd. from BzH and $NH_2CONHNHPh$; it also reacted with PhNCS on long

contact, yielding the thiosemicarbazone, m. 189°, also identical with that made directly from BzH. Unlike B, PhCH:NNH_2, reacted readily in Et_2O with Ph_2C:CO, yielding *benzaldehyde diphenylacetylhydrazone*, m. 196° after recrystn. from AcOH. PhMeC:NNH_2 (D), m. 24–5° when recrystd. from Et_2O and petr. ether, showed a tendency to form double mols. in C_6H_6. The phenylsemicarbazone, m. 187–8°, obtained by the action of PhNCO on D in Et_2O was identical with that prepd. from PhCOMe and $NH_2CONHNHPh$. PhNCO did not react as energetically with Ph_2C:NNH_2 as it did with the above hydrazones. The benzophenone phenylsemicarbazone was identical with that made directly from Ph_2CO, likewise, the action of Ph_2C:CO on Ph_2C:NNH_2 was not lively. The product, *benzophenone diphenylacetylhydrazone*, m. 151–2° after recrystn. from alc. The diminished reactivity of the NNH_2 group is again noted in fluorenone hydrazone which must be warmed on the H_2O bath with PhNCO in Et_2O in order to obtain the *fluorenone phenylsemicarbazone*, m. 222° (recrystd. from AcOH), difficultly sol. in alc. and C_6H_6, identical with the product synthesized directly from fluorenone. Benzil hydrazone reacted very slowly with PhNCO; by boiling in C_6H_6, the *phenylsemicarbazone* was obtained, m. 167–9°, identical with the compd. prepd. directly from benzil and $NH_2CONHNHPh$. **XXII. The reduction of diazoacetic ester.** H. STAUDINGER, L. HAMMET AND J. SIEGWART. *Ibid* 228–38.—The search for the hydraziacetic ester, stated to have been obtained by Curtius (*Ber.* **27**, 775(1894)), has been continued without success. Every supposedly hydrazi compd. obtained thus far has on closer examn. proved to be a *hydrazone*. On reducing N_2CHCO_2Et with H_2S in the presence of NH_3, the product formed consisted of a liquid and a solid. In this liquid portion the authors at first believed that they had finally found the long-sought hydraziacetic ester. However, a study of the chem. and physical properties of both the liquid and solid products proved them to be *stereoisomers* of the same *hydrazone, viz., syn-ethyl glyoxylate hydrazone* (A) and *anti-ethyl glyoxylate hydrazone* (B). On long standing, (3–5 days), or sooner by warming, an equil. is established between the 2 forms; the equil. mixt. is estd. as consisting of ⅓ A and ⅔ B. While many of their general reactions are similar, A and B possess some distinctly different properties by which they are distinguished. Thus, A is a liquid which does not solidify at −20°, $b_{0.2}$ 38–40°, is not associated in a C_6H_6 medium, is difficultly sol. in H_2O, reacts slowly with PhNCO and not at all with Ph_2C:CO. In contrast, B is a solid, m. 38–0.5°, $b_{0.1}$ 105–6°, is strongly associated in C_6H_6, dissolves very readily in H_2O, reacts almost violently with PhNCO and easily with Ph_2C:CO. The other properties of the 2 isomers are described under the following summary of the methods of prepn. No marked reaction was noted when H_2S was led for 4 days into an alc. soln. of N_2CHCO_2Et. Reduction did take place when 1 cc. of 2 *N* NH_4OH was added daily to the alc. soln. of the N_2CHCO_2Et while H_2S was being passed in. The reaction mixt. was filtered from the free S and the residue extd. with Et_2O-petr. ether. A was obtained from the ether-sol. portion by vacuum distn. (ca. 8–10 g. from 30 g. N_2CHCO_2Et), and purified by further distn. It is a colorless, odorless, mobile liquid, $b_{0.2}$ 38–40° and b_{13} 82° (with slow decompn.), easily sol. in org. solvents and slightly sol. in H_2O. A is not very stable; it gradually becomes viscous on standing, rearranging itself partially into B. The 2 isomers can be sepd. by distg. *in vacuo*. B is very sol. in org. solvents, likewise in H_2O. Mol. wt. detns. in C_6H_6 by the f. p. method gave values of 135–219. Both isomers are split up into glyoxylic ester and $NH_2NH_2.HCl$ by concd. HCl. Dil. H_2SO_4 reacts analogously. Treated with BzH, benzalazine is obtained from both but no stereoisomeric benzal compds. could be isolated. Again, both yielded N_2CHCO_2Et when treated in petr. ether with HgO, part of the diazoacetic ester forming the Hg salt. By prolonged heating at 200°, both hydrazones evolved N and were at least partially converted to AcOEt. A reacts very slowly with PhNCO; after several hrs.' standing, the *phenylsemicarbazone*

sepd. out as a cryst. mass, difficultly sol. in H_2O and Et_2O; recrystd. from hot C_6H_6 or alc., colorless crystals m. 128–30°. PhNCO reacts so energetically with B that it is best to carry the reaction out in Et_2O with cooling. The *anti-phenylsemicarbazone* crystd. out instantaneously, colorless crystals from alc. m. 176°, less sol. in C_6H_6 than the *syn*-compd. The phenylsemicarbazone prepd. directly from glyoxylic ester and $NH_2CONHNHPh$ is identical with the *anti*-compd. and contains none of the *syn*-isomer. A did not react with $Ph_2C{:}CO$ but when the calcd. amt. of the latter was added to B in Et_2O, the *anti-diphenylacetylhydrazone of ethyl glyoxylate* was formed in nearly quant. yield, colorless crystals from alc. m. 178°. *syn*-Camphorquinone hydrazone showed no tendency to associate in C_6H_6 according to f. p. measurements. The *anti*-compd. was too insol. in C_6H_6 for mol. wt. detns. **XXIII. Formulation of diazoacetic ester and diazo anhydride.** H. Staudinger. *Ibid* 239–41.—For reasons made evident in the foregoing communications, S. rejects the Curtius formula (I) for aliphatic diazo compds. In the present paper 2 other assumptions are considered, (*a*) that they are diazo anhydrides, *i. e.*, derivs. of oxdiazole (II), or (*b*), they have the structure assigned to them by Angeli and Thiele (III). After a discussion of both



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theories, S. concludes that the Angeli-Thiele formula is the most satisfactory in explaining the behavior of aliphatic diazo compds. A. T. Frascati

Manufacture of chloroform from ethyl alcohol and the mechanism of its reaction. Shuichirō Ochi. *J. Chem. Ind. Japan* **24**, 209–28(1921). —In order to det. the mechanism of the reaction of hypochlorite on EtOH in the manuf. of $CHCl_3$, O. investigated the reaction products, passing 1900 cc. of Cl into 100 cc. of 10% EtOH, containing 6 g. of CaO, at 60°. Of 3 theories proposed by Liebig, Goldberg, and Dott, O came to the conclusion that in the main reaction, L., *i. e.*, $2C_2H_6O + 8CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + Ca(CHO_2)_2 + 5CaCl_2 + 2H_2O$. However, 0.75 of the HCO_2H is decompd. into CO_2 and H_2O by the further oxidation and 0.25 remains unchanged. The quantity of EtOH to be used is about ⅔, the greater part of the remainder changing into AcOH. The explosive reaction in its manuf. is due to violent evolution of O by decompn. of hypochlorite at a high temp., not to CO_2. To avoid this, the use of a lower temp. is essential. The preferable way is, according to O., to pass Cl into the mixt. of EtOH and milk of lime, regulating its temp. under the following optimum conditions: 60°, concn. of alc. 10%, $Ca(OH)_2$ about 300 g. in 1 l. of dil. alc.; Cl 0.75–0.87 mol. for each mol. of $Ca(OH)_2$. In this process, 63.5–65.5% of Cl and 54.4–54.9% of alc. are utilized. MgO, BaO, NaOH, and KOH give a smaller yield than CaO. The method of purification of the crude product to a degree acceptable to the Japanese pharmacopoeia is given. S. T.

Alcoholysis. IV. Alcoholysis of esters of unsaturated acids and of the corresponding saturated esters. B. Dasannacharya and J. J. Sudborough. *J. Indian Inst. Sci.* **4**, 181–203(1921); cf. *C. A.* **14**, 3652.—Close relationships between processes of esterification, alcoholysis and hydrolysis of esters have been shown. Kolhatkar (*C. A.* **9**, 2762) showed that the relative rates of esterification by the catalytic method and of alcoholysis of the corresponding Et esters by means of HCl follow the same order. He showed that the relative affinities of the Et and Me groups toward an acyl group are to a large extent independent of the nature of the acyl group, a conclusion drawn by Hemptinne (*Z. physik. Chem.* **13**, 564(1894)) and Lowenburg (*Ibid* **15**, 389(1894)), and

Meyer (*C. A.* **3**, 1864) by a study of the hydrolysis of the Me, Et, Pr and Bu esters of the various acids by means of HCl. B. Bhagvat, K. Bhagvat, and S. (*J. Indian Inst. Sci.* **2**, 121(1918)) showed that in the absence of a catalyst esters of strong acids undergo alcoholysis more readily than esters of weak acids, just as by the process of direct esterification strong acids are esterified more rapidly than weak acids, and S. and Karve (*C. A.* **14**, 3652) showed that two *o*-substituents in the acyl portion of an aromatic ester inhibit alcoholysis when Na alkyl oxides or mineral acids are used as catalysts, just as these substituents inhibit esterification (Meyer and S., *Ber.* **27**, 510, 1580, 3146(1894)) by the catalytic process or hydrolysis of aromatic esters by mineral acids (Meyer, *Ber.* **28**, 188(1895)). According to Roberts and S. (*J. Chem. Soc.* **87**, 1842(1905)), Thomas and S. (*C. A.* **2**, 68), Gittins and S. (*C. A.* **3**, 2118) an acid with an α,β-unsatd. linking is esterified far more slowly than its satd. analog when the catalytic method is used and T. Williams and S. (*C. A.* **6**, 2064) showed that the Et esters of α,β-unsatd. acids are hydrolyzed much more slowly than the esters of the corresponding satd. acids. D. and S. desired to ascertain whether an α,β-unsatd. linking in the acyl portion of an ester has a pronounced retarding effect on alcoholysis, using HCl as a catalyst. Two series of detns. of the velocity consts. of alcoholysis of esters of α,β-unsatd. acids and esters of the corresponding satd. acids were made. In one series the dilatometric method similar to that used by Kolhatkar was used and in the other a polarimetric method was used. The results obtained by the first method are reported here. The series of reactions studied were (*1*) $PrCO_2Me + EtOH \longrightarrow PrCO_2Et + MeOH$; (*2*) $MeCH{:}CHCO_2Me + EtOH$; (*3*) $PhCH_2CH_2CO_2Me + EtOH$; (*4*) $PhCH{:}CHCO_2Me + EtOH$ and the corresponding reverse reactions. The esters were prepd. by the Fischer-Speier method of esterification or by the action of alkyl iodides on the Ag salts, using C_6H_6 as a diluent. A soln. of 10 mols. alc. to 1 of ester and the same vol. of alc. HCl free from atm. moisture were used in filling the dilatometers, a description of which is given. The thermostat contained duplicate dilatometers of the same shape and size as the first set. The second set contained alc. HCl but no esters. HCl acts on alc. with formation of alkyl chlorides, a reaction which causes a change in vol. and a correction must be applied for this. In these expts. about 20 mols. alc. were present to one of ester so that the reaction is practically monomol. The values of K for the reactions: $PrCO_2Me + EtOH \longrightarrow PrCO_2Et + MeOH$ and $PrCO_2Et + MeOH = PrCO_2Me + EtOH$ do not check those found by Kolhatkar. Values taken from a table given show that esters containing an α,β-olefin linking in the acyl group undergo alcoholysis far less readily than esters of the corresponding satd. acids. $\frac{K\text{Me Butyrate}}{K\text{Me Crotonate}} = 13.6$ and the av. for the 4 cases is 16.5. Although the α,β-linkage has a marked retarding effect on the alcoholysis the effect is not so great as in esterification, where the mean value for 3 pairs of acids is 42 as compared with a value 29.5 for hydrolysis of the esters with HCl. A comparison of the alcoholysis consts. shows that the rate is decreased by replacing a β-Me group by Ph. The ratio of the consts. for the direct and reverse reactions is roughly independent of the nature of the acyl group. H. E. Williams

Thioamides. I. Preparation of thioamides with the aid of aluminium sulfide. Karl Kindler and Friedrich Finndorf. Univ. Hamburg. *Ber.* **54B**, 1079–80 (1921).—Al_2S_3, prepd. by the method of Fonzes-Diacon (*Compt. rend.* **130**, 1314(1900)), is allowed to react on acid amides in the presence of hydrated salts in sealed tubes at a high temp. in such proportions that an excess of H_2S is formed. Instead of the amide may be used the NH_4 salt of the acid, in which case the use of a hydrate is not necessary. Thus, 2.5 g. $BzNH_2$, 7.5 g. Al_2S_3 and 1.3 g. $Na_2SO_4.6H_2O$ heated 1.5 hrs. at 240–50°, then dried, extd. in a Soxhlet with Et_2O and crystd. from H_2O, yield quant. perfectly pure $PhCSNH_2$, m. 115–6°. $AcONH_4$ heated 1 hr. at 240° with 5 parts Al_2S_3 yields

$MeCSNH_2$, m. 116°. **II. Reduction of thioamides to primary amides.** KARL KINDLER AND WALTER DEHN. *Ibid* 1080–1.—By the use of Al-Hg in a neutral medium thioamides can be reduced to the corresponding primary amines with good yields. Thus, 0.1 mol. $PhCSNH_2$ in 4 parts 99% alc. and 13 g. Al-Hg slowly treated under a reflux with turbining with 13 cc. H_2O, heated 3 hrs. at 60–70°, made alk. with NaOH, distd. with steam, acidified with HCl, concd., decompd. with concd. KOH, taken up with Et_2O and dried with K_2CO_3 give $PhCH_2NH_2$, b. 184.5°. $MeCSNH_2$ (1 g.) in 10 cc. of 90% alc. similarly reduced with 1 g. Al-Hg and 1 cc. H_2O gives $EtNH_2$.

CHAS. A. ROUILLER

The mixed anhydrides of sulfuric and carboxylic acids. I. Acetylsulfuric acid. A. J. VAN PESKI. Pernis. *Rec. trav. chim.* **50**, 103–18(1921).—The technical methods of prepg. Ac_2O use chiefly Cl compds. but v. P. has succeeded in using SO_3 (Ger. pat. 275,846 and 286,872). v. P. has also found that when SO_3 acts on AcOH below 0° acetylsulfuric acid (**A**) is formed, which gives salts. Anhydrous NaOAc added to **A** gives the Na salt of **A** (**B**) which is little sol. in AcOH. **B** heated alone decomps., giving Ac_2O and $Na_2S_2O_7$ but heated in AcOH reacts thus: $AcNaSO_4 + AcOH \longrightarrow Ac_2O + NaHSO_4$. This reaction is reversible and equil. occurs well to the left, but may be moved to the right by removing one of the products. Other anhydrides were prepd. similarly. Franchimont (*Verslag. Akad. Wetensch. Amsterdam* **16**, 368(1881)) first obtained **A** by mixing equiv. amts. of Ac_2O and H_2SO_4. When equiv. amts. of Ac_2O and H_2SO_4 are heated together at 70° the liquid becomes yellow-brown and the course of the reaction can be traced by detg. the H_2SO_4 present by titration (**A** after decompn. by H_2O neutralizes 3 equivs. of acid while H_2SO_4 neutralizes but 2). At the end the H_2SO_4 present indicates 70% transformation while the total acidity indicates 93%. On adding $PhNH_2$ before titrating less alkali is required, owing to the formation of PhNHAc and as the transformation advances this difference in the alkali required gradually disappears in spite of the fact that 30% of the H_2SO_4 remains unchanged. The liberation of CO_2 furnishes the explanation since this is associated with the formation of sulfoacetic acid (**C**). **C** is acetylated at the CH_2 group with **A**, giving acetylsulfoacetic acid (**D**) and H_2SO_4. **D** then decomps., giving sulfoacetone and CO_2. This reaction is of only secondary importance. v. P. found an acid, $C_8H_8O_{10}S_2$, after the sepn. of **C**, which can be formed by the union of 2 mols. of **D** with the elimination of 2 H_2O. This acid is thought to be disulfodehydracetic acid (**E**), which is dibasic. Further heating of **E** transforms it into dark colored sulfo acids. If in the transformation of **A** an excess of Ac_2O is used the H_2SO_4 liberated by the accessory reactions always forms additional **A** until all H_2SO_4 has been converted into sulfo acids. The action of SO_3 on AcOH has already been studied by Melsens (*Ann.* **52**, 276(1844)). $AcCl + H_2SO_4$ forms an addition product from which HCl seps. only at such a high temp. that **A** at first formed is converted into **C**, etc. The reaction between the Na salt of **A** and AcOH is reversible so that this salt is obtained by treating $NaHSO_4$ with Ac_2O at low temps. The Na salt of **A** is prepd. more rapidly by the action of **A** on NaOAc or by adding oleum or H_2SO_4 dropwise to a suspension of NaOAc in Ac_2O dild. with AcOH, which permits of working at a higher temp. Owing to the great increase in the velocity of acetylation with Ac_2O caused by the addition of H_2SO_4 v. P. has examd. the action of **A** on some compds. $PhNH_2$ is immediately acetylated. Compds. difficult to acetylate, like $Br_3C_6H_2OH$, $Br_3C_6H_2NH_2$ and BzH, were acetylated well even at 0°. With AmOH $AmHSO_4$ was obtained; it was isolated as the Ba salt. With PhOH AcOPh and probably some Ph_2SO_4 were formed. Since **A** as obtained always contains about 30% AcOH v. P. detd. whether the reaction $AcHSO_4 + AcOH \longrightarrow Ac_2O + H_2SO_4$ is of significance in acetylations with **A** and found that it takes place to some extent. Expts. were done in order to det. whether **A** can sulfonate aromatic hydrocarbons.

Tests made by agitating **A** for a long time with C_6H_6 at 10° gave $PhSO_3H$. Into an iron app. of which the cover and interior were nickeled, provided with an agitator and a thermometer, 125 g. SO_3 in 240 g. 100% AcOH were distd. while the temp. was kept below 0°. **A** was obtained in AcOH soln. as a thick nearly colorless liquid. The same product was obtained on adding 170.6 g. oleum (66.3% free SO_3) to 229.3 g. of 26% Ac_2O at −7° to −2°. The above mixt. when heated at 70° is transformed into **C**, concerning which details are given. 150 g. 60% Ac_2O treated slowly with agitation with 21.5 g. 100% H_2SO_4 at −5° to −10° and then with 20.5 g. anhydrous AcONa was kept cold until the next day and when treated with 400 cc. dry Et_2O gave a ppt. from which the Et_2O was sepd. by decantation. This was repeated 4 times with 200 cc. Et_2O and gave finally 40 g. of the Na salt of **A** as a white powder that decomps. in H_2O, giving $NaHSO_4$ and AcOH. 65 g. anhydrous Na_2SO_4 in 165 g. warm glacial AcOH was cooled to 50° and treated dropwise with 73.5 g. 100% H_2SO_4 at 60° or less. After cooling slowly to room temp. the mixt. was cooled with ice and 285 g. Ac_2O (96%) were added with agitation. After 1 week on ice with occasional agitation the Na salt of **A** was sepd. as described above. 20.5 g. anhydrous NaOAc in 150 g. 33.9% Ac_2O was treated with 24.5 g. 100% H_2SO_4 at 8–10°; this gives a supersatd. soln. of the Na salt of **A**, from which it may be crystd. on cooling and the sepn. finished with Et_2O: a 90% yield was obtained. This was the most convenient method used. To 20.5 g. anhydrous NaOAc in 150 g. 22.5% Ac_2O after cooling was added 21.35 g. oleum (66.3% SO_3) at 8–10°. After standing all night at 8–10° the crystals were sepd. and the soln. worked up with Et_2O, giving a 97.2% yield of the Na salt of **A**. 20 g. of the Na salt was heated in a flask with occasional agitation up to 220° and gave 5.2 g. distillate containing 72.6% Ac_2O (64% yield) and 14.6 g. residue; 20% of the Ac_2O was recovered as AcOH. The residue besides $Na_2S_2O_7$ contained $MeSO_3Na$ derived from the Na salt of **C** by the loss of CO_2. Of **A** prepd. from 240 g. 100% AcOH and 160 g. SO_3 200 g. was added gradually to 164 g. finely powdered NaOAc with some cooling with ice. On distn. 210 g. 33.4% Ac_2O (69.6% yield) were obtained. To **A** prepd. from 54.85 g. 92.9% Ac_2O and 52 g. 100% H_2SO_4 were added 44 g. iso-AmOH below 0°. The H_2SO_4 was pptd. with $BaCO_3$ and the filtrate was treated with $BaCO_3$ until Congo paper was no longer colored blue; then the soln. was concd. *in vacuo* and sepd. 54.5 g. Ba isoamylsulfate. E. J. WITZEMANN

Derivatives of δ- and ε-amino acids. L. RUZICKA. *Helvetica Chim. Acta* **4**, 472–82 (1921).—As starting material for the prepn. of compds. resembling quinine R. prepd. $MeNH(CH_2)_4CO_2H$ (**A**) according to the method of Fischer and Bergmann (*C. A.* **7**, 2541) by methylating p-$MeC_6H_4SO_2NH(CH_2)_4CO_2H$ in alk. soln. with MeI but the method was abandoned. The lactam of **A**, *viz.*: *N*-methyl-α-piperidone (**B**) was prepd. by catalytically reducing *N*-methyl-α-pyridone (**C**). **B** was then easily transformed into **A**. In prepg. $MeNH(CH_2)_5CO_2H$ (**D**) the method of Thomas and Goerne (*C. A.* **13**, 2024), consisting in methylating p-$MeC_6H_4SO_2NH(CH_2)_5CO_2H$ with MeI, might have been used. It is simpler to treat *cyclohexanone isoxime* (**J**) with Na and Me_2SO_4 to form $CH_2.CH_2.CH_2.CH_2.CH_2.NMe.CO$. 90 g. freshly distd. **C** in 200 cc. H_2O were treated with 10 g. Pt black and H_2 during 2 or 3 days with agitation. The Pt was then filtered, the H_2O was removed *in vacuo*, and the residue on distn. gave **B** quant. as a colorless oil b_{14} 104°. Fischer and Bergmann prepd. it by heating **A** (*C. A.* **7**, 2541). **B** was heated for 1 day with concd. HCl, the soln. was evapd., HCl was removed with Ag_2O and the excess of Ag with H_2S. The filtrate when evapd. *in vacuo* at 50° and dried gave **A**, m. 126–7° from abs. alc. and ether (F. and B. stated 121°). *N-Ethyl-α-piperidone* (**E**), a colorless liquid with faint odor, b_{12} 107–8°, was prepd. by the catalytic reduction of *N*-ethyl-α-pyridone. 5 g. **E** in abs. alc. when treated with

35 g. Na and 350 g. alc. gave after steam distn. a soln. which was treated with HCl. The acid soln. on evapn. and treatment with KOH and ether extn. gave a thick oil b_{12} 120–5°, which turned brown in the air and had an odor resembling nicotine. The analysis agreed with the formula $(CH_2.NEt.CH_2.CH_2.CH_2.C=)_2$, formed by the condensation of 2 mols. of **E**. Wallach noted similar reactions (*Ann.* **324**, 285(1902)). **E** when treated in a similar way gave δ-ethylaminovaleric acid (**F**), prisms m. 138–9° from alc.-ether mixt. **F** as the HCl deriv. in a little H_2O gave with BzCl the *benzoyl derivative* (**G**), m. 97–8°, and ethyl δ-benzoylethylaminovalerate (**H**) was prepd. by treating **F** with alc. HCl and to the *ester* so formed an excess of BzCl in C_6H_6 was added. The mixt. after 24 hrs. heating gave off HCl and the excess of BzCl was decompd. with H_2O. **H** was extd. with ether, a colorless oil, $b_{0.5}$ 165°. 10 g. cyclohexanone oxime with 20 cc. H_2SO_4 (1 l. H_2SO_4 with 200 cc. H_2O) were heated until a brisk reaction set in and the mixt. was then iced, made alk. with 30% NaOH, at a temp. below 10°, and filtered from Na_2SO_4, and the filtrate when ether-extd. gave 66% of the theoretical yield of cylcohexanone isoxime (**J**), b_{12} 140°. 10 g. **J** with 2.2 g. Na in 50 cc. xylene were allowed to stand for 1 day and then 13.6 g. BzCl were added and the reaction mixt. after standing several days when heated on the steam bath gave *N*-benzoylcyclohexanone oxime, a thick oil, b. 150°, which soon solidified, m. 45–7°. *Ethyl ε-benzoylaminocaproate* (**K**) was prepd. from $BzNH(CH_2)_5CN$ (**M**), which was made according to the method of Braun (*Ber.* **37**, 2915(1904)) and Gabriel (*C. A.* **3**, 2137) modified by R. 1100 g. benzoylpiperidine in 4 portions with 1200 g. PCl_5 were refluxed 1.5 hrs., then poured on ice and the aq. layer was sepd. The crude 1,5-benzoylaminochloropentane was air-dried, and heated 15 hrs. in 4 l. alc. with 700 g. KCN in 1400 cc. H_2O. Half of the alc. was distd. and the residue when treated with H_2O yielded a dark brown solid **M**. This was esterified by heating for 24 hrs. with alc. HCl, concd., treated with H_2O and C_6H_6 and filtered. The C_6H_6 soln. was shaken with soda, and the neutral product when distd. *in vacuo* gave 575 g. **K** $b_{0.1}$ 184–6°, m. 35°. *Ethyl-α-aminocaproate* (**L**) was prepd. in 2 ways. **J** was sapond. during 4 hrs. with concd. HCl and the soln. was evapd. to dryness. The residue after sapon. with alc. HCl and removal *in vacuo* of the excess of HCl gave crystals which on treatment with KOH in the presence of ether gave **L**, a colorless oil, $b_{1.6}$ 80–1°. On long standing it became solid and polymerization took place (the product could not be distd). By the 2nd method **M** was heated several days with concd. HCl, then treated with water, the BzOH was filtered, the soln. was evapd. to dryness and *ε-aminocaproic acid hydrochloride* was obtained. This was treated in the same way as by method 1. The methylation of **J** by heating with CH_2O did not succeed; consequently a C_6H_6 soln. of **J** was treated with 1.1 mol. powdered Na in the cold, H_2 was evolved and the voluminous *sodium derivative* sepd. after standing 2 days, and it was then treated gradually with 1.1 mols. Me_2SO_4 and after 2 days 0.5 mol. each of Na and Me_2SO_4 were added. $NaMeSO_4$ was removed, washed with C_6H_6 and the washings and the main soln. were distd. H_2O and KOH caused the sepn. of *N-methylcyclohexanone isoxime* (**N**), b_{11} 104–6°. The speed of formation of this compd. could not be increased by heating and high boiling condensation products resulted. *ε-Methylaminocaproic acid* (**O**) was prepd. by heating for 1 day a mixt. of **N** and concd. HCl. The residue crystd. after evapn. in a vacuum desiccator; it is very hygroscopic. Ag_2O was added to remove HCl; the cryst. NH_2 acid m. (closed tube) 130–1°. *Ethyl ε-benzoylmethylaminocaproate* (**P**) was prepd. by heating for 8 hrs. an alc. soln. of HCl and **O** and the *ester hydrochloride* was heated for 10 hrs. with an excess of BzOH. This is a thick colorless oil, b_6 170°. **P** could not be methylated by heating it in xylene with Na and Me_2SO_4.

H. E. Williams

Esters of γ-chloroacetoacetic acid. J. F. Hamel. *Bull. soc. chim.* **29**, 390–402

(1921).—H. reviews the literature on the synthesis of the esters and records the following syntheses: (*a*) In dry ether. (*1*) Methyl γ-chloroacetoacetate, $ClCH_2COCH_2CO_2Me$, was prepd. by adding slowly $ClCH_2CO_2Me$, 108.5 g., in an equal vol. of dry Et_2O to 12 g. Mg and 0.5 g. $HgCl_2$ and heating under reflux 2 hrs. on a water bath. After the addition of dil. H_2SO_4, the ether-sol. reaction products were sepd. and recovered by the distn. of the ether. Unchanged $ClCH_2CO_2Me$ being removed by fractionation, there was obtained crude $ClCH_2COCH_2CO_2Me$ b_{11} 92–100°, purified through the Cu deriv. obtained by agitating the ester with satd. $Cu(OAc)_2$; crystd. from C_6H_6, the Cu deriv., m. 173–4°. It is decompd. by the theoretical amt. of dil. H_2SO_4. The pure ester is a colorless liquid irritating to the nostrils and skin, b_{11} 96–7°, d_4^0 1.3048, n_D^{19} 1.4590, mol. ref. 31.53 (calcd. 32.41). (*2*) $ClCH_2COCH_2CO_2Et$ (**A**) was prepd. from 1 mol. of Mg and 2 mols. of $ClCH_2CO_2Et$ as described in (*1*). The crude reaction product, b_{12} 100–3°, equaled 56% of the theory. The purified **A** is colorless, irritating to the eyes, almost insol. in H_2O, miscible with org. solvents, b_{12} 102°, b_{760} about 210° (decompn.), m. −8°, d_4^0 1.2292, n_D^{17} 1.45452, mol. ref. 36.71 (calcd. 36.28). The Cu deriv. $[ClCH_2COCH(CO_2Et)]_2Cu$, prepd as in (*1*), gives green needle-like crystals from benzene, m. 167.5°, decomps. above 160°. The analogous Ni compd., pptd. from a mixt. of the ester and $Ni(OAc)_2$ when NH_4OH is slowly added, is green, m. 131–2°. The Zn deriv. similarly prepd. is white and cryst., m. 121°. Mg deriv. m. 170°, is insol. in org. solvents save MeOH. Similar Al, Mn, Pb, Bi and Co derivs. were prepd. **A** heated with thiourea in a little alc. on the water bath yielded ethyl aminothiazylacetate, $EtCO_2CH_2C{:}CH.S.C(NH_2){:}N$, as the HCl salt. Set free with NH_3 the base is cryst., yellow, m. 95.5°. Hydrolyzed with HCl, the ester yielded CO_2, $ClCH_2COMe$ and EtOH. (*3*) Isobutyl γ-chloroacetoacetate (**B**), $ClCH_2COCH_2CO_2CH_2CHMe_2$, prepd. from $ClCH_2CO_2CH_2CHMe_2$ by the method of (*1*), was contaminated with iso-BuOAc, much unchanged iso-BuO_2CCH_2Cl and iso-BuOH. The **B** obtained was 29% of the theoretical amt., b_{11} 118°, d_4^0 1.1426, n_D^{17} 1.45212, mol. ref. 45.46(45.92). The Cu deriv. m. 126.5°. (*b*) Without ether. **A** was obtained with a yield of 5% without the use of ether or other solvent by using Mg-Hg. In benzene the yield was lower still, but in dry alc.-free $CHCl_3$ the yield was 48%. (*c*) With Al-Hg **A** was prepd. in 15% yield from $ClCH_2CO_2Et$ after the method of Doht and Weisl (no reference cited; see Picha, *Monatsh.* **1906**, 1245). AcOEt in small quantities was found to be a product of the reaction. R. L. BROWN

The velocity of hydration of anhydrides of dicarboxylic acids. I. Introduction. P. E. VERKADE. Univ. Commerciale Néerlandaise, Rotterdam. *Rec. trav. chim.* **40**, 192–8(1921).—Voerman (*Ibid* **23**, 265(1904)) began a systematic study concerning the stability of the anhydrides of di-CO_2H acids toward water to establish proof of the accuracy of the Baeyer strain theory, the results of which were of little importance. All attempts to obtain anhydrides of oxalic and malonic acids have failed; Einhorn and Diesbach (*C. A.* **2**, 1696), Staudinger (*C. A.* **2**, 2808, 3829(1908)) and Ott (*C. A.* **8**, 333) obtained dialkylmalonic anhydrides. In these latter derivs. the alkyl groups stabilize the anhydride. The velocity consts. for the hydration of succinic and glutaric acid anhydrides are said by Voerman to verify B.'s strain theory but the differences are within the limits of error according to V. Voerman also examd. the higher anhydrides of this series C_6 to C_{10} and found them to be too little sol. in H_2O for the electrometric method and considerably mol. associated by the b. p. method. The tension theory of Baeyer and van't Hoff involving const. and directed C valences requires some modification to conform with the more recent conceptions of valence such as those of Werner, Böeseken, Stark, etc., which consider that the groups bound to C influence each other mutually. Such considerations lead irrevocably to a tetrahedral asym.

C atom (cf. Holleman, *C. A.* **8**, 1363). Böeseken (*C. A.* **6**, 1610) thought that the question as to whether the C atom is a regular or asym. tetrahedron could be detd. experimentally by observing "whether the introduction of an atom or a group or even of an unsatd. bond in the one or the other mol. containing a ring of atoms influences the tension of the ring." But V. shows that this proof would be of value only if the truth of 2 hypotheses, which B. does not even mention, is granted. Böeseken (*Verslag Akad. Wetenschappen, Amsterdam* **14**, 622(1911); *C. A.* **6**, 1610) started to measure the velocity of hydration of anhydrides of di-CO_2H acids in aq. soln. and soon found that other factors than B.'s strain theory are involved. In studying the velocity of hydration of higher fatty acid anhydrides V. found (*C. A.* **11**, 2897; **8**, 2346) the velocity with which the anhydride unites with H_2O to give an addition product was measured and not the the rate of acid formation. The same may prove to be true of the di-CO_2H acid anhydrides and certainly nothing could be detd. about tension in the ring until it had been shown that the velocity of acid formation can actually be measured in these cases. Detns. of velocity of hydration of cyclic anhydrides can yield nothing concerning the configuration of the tetrahedral C atom because our ideas concerning "the tension" in ring systems are too vague, and we do not even know that it always exists. Moreover, the relation between velocity of the opening of a ring and any tension there may be in the ring has not been established. After data on velocity of hydration are in hand more can be said about the mechanism of hydration of cyclic anhydrides. The introduction of Me into succinic anhydride diminishes considerably its stability toward H_2O; an Et group has slightly the opposite effect; the introduction of another Me beside the first greatly increases the stability. The influence of other groups may be studied similarly. Possibly the relation observed by Wilsdon and Sidgwick (*C. A.* **8**, 906) that the rate of hydration and the dissociation const. show a general tendency to rise and fall together may as they suggested have exceptions. **II. Methylated succinic anhydrides.** *Ibid* 199–20.—In the exptl. part of this paper many bibliographic and other data have been assembled, which can not be satisfactorily abstracted, concerning the velocity of hydration of anhydrides of succinic acid and its Me deriv. The new results on the velocity of hydration and the old and new results on the dissociation consts. are summarized thus:

	k^{25}.	0.4343 k^{25}.
Succinic acid	6.52×10^{-5}	0.0692
Monomethylsuccinic acid	8.36	0.0985
Dimethylsuccinic acid asym.	8.25	0.0762
Dimethylsuccinic acid sym. 128°	1.33×10^{-5}	0.110
Dimethylsuccinic acid sym. 208°	1.94	0.153
Trimethylsuccinic acid — —	3.02	0.0783
Tetramethylsuccinic acid — —	3.13	0.00638

In order to draw conclusions from the numerical data it is necessary to wait for the data on the methylmaleic acid anhydrides. For the present until these data are completed the following points may be brought out. (1) The dialkylmaleic acids, *e. g.*, dimethylmaleic acid (pyrocinchonic), diethylmaleic acid (xeronic) and methylethylmaleic acids have been sepd. in the solid state only as anhydrides. On acidifying the aq. soln. of a salts of these acids the acids at first formed are sepd. at once as the anhydrides. These anhydrides dissolved in H_2O are incompletely hydrated so that Rivett and Sidgwick (*C. A.* **4**, 2900) have expressed the facts by the equil.: anhydride + $H_2O \rightleftarrows$ acid, which at 25° moves strongly toward the anhydride side. This possibility was not excluded in the case of the anhydride of tetramethylsuccinic acid, but it was noted that a notable amt. of the anhydride is not present at 25°, as was shown by the cond. detns. When the dil. solns. of these acids are distd., however, the corresponding anhydride

passes with the vapor. (2) At 25° the hydration of the anhydrides of the methylated succinic acids is monomol.; succinic anhydride at 0° shows an irregularity similar to that observed by Böeseken *et al.* (*C. A.* **6**, 1610) with the anhydride of β-acetoglutaric acid. (3) V. previously found that anhydrides of satd. di-CO_2H acids are associated in certain solvents, and that this tendency is less for anhydrides of succinic and glutaric acids (Böeseken, v. d. Eerden, *C. A.* **9**, 445) than for higher anhydrides. It is, however, not impossible that the following reactions may occur: (1) polymerized anhydride ⟶ simple anhydride; (2) simple anhydride + H_2O ⟶ acid. If the velocity of (2) is great in comparison with that of (1) the increase in cond. measured in the aq. solns. is the velocity of (1), *i. e.*, the velocity of monomerization. This is not probable owing to the considerable soly. in H_2O of these anhydrides but it may be tested experimentally and f. p. data are given showing that succinic anhydride is not associated in aq. soln. V. concludes that this is also true of all the succinic acids here investigated. (4) Hjelt (*Ber.* **26**, 1925(1893)) investigated the tendency of various succinic acids to form anhydrides and it would be interesting to compare his results with these on their hydration, but V. found that decompn. (ketodilactone formation) occurs and for other reasons the results of H. are of no value for this purpose. E. J. WITZEMANN

Acidity of the hydrogen atoms of uric acid. HEINRICH BILTZ AND LISBETH HERRMANN. Univ. Breslau. *Ber.* **54B**, 1676–94(1921).—Solns. were prepd. of uric acid and of each of its 4 mono-Me, 6 di-Me, and 4 tri-Me derivs. The p_H of each of these 15 solns. was detd. by means of indicators, and the dissociation const. K was then calcd. for each acid. The value of K, in terms of 10 to the —5th power, was: *uric acid* 13; *trimethyluric acids;* 1,3,7 2.9; 1,3,9 0.13; 1,7,9 10.0; 3,7,9 0.17; *dimethyl uric acids;* 1,3 1.8; 1,7 6.2; 1,9 7.3; 3,7 3.2; 3,9 0.21; 7,9 7.9; *monomethyl uric acids:* 1 4.7; 3 4.5; 7 11.5; 9 22.0. The values of K for the trimethyluric acids showed that the H atom at 3 had the greatest inclination to electrolytic dissociation, and was followed in descending order, by the H atoms at 9, 1 and 7, resp. This deduction was supported by the values of K for the dimethyluric acids. The presence of the Me group had but slight influence on the ability of the H ion to become dissociated. Thus 3,9-dimethyl- and 1,3,9- and 3,7,9-trimethyluric acids, which had no H in 3 and 9, had almost the same value for K. A discussion of the alkylation of uric acid by various procedures is appended. JOSEPH S. HEPBURN

Some amides of acids of the sugar group. Contribution to the knowledge of the relation between constitution and rotatory power. W. E. VAN WIJK. Univ. Leyden. *Rec. trav. chim.* **40**, 221–46(1921).—Miss van Marle recently (*C. A.* **15**, 364) published results confirming the rule of Hudson (*C. A.* **11**, 1426) that the position of the OH group with respect to the α-C atom of monobasic acids of the sugar group dets. the sign of rotation of the phenylhydrazide. v. W. has continued this work which confirms this rule and at the same time has verified the rule of Chugaev (*Ber.* **31**, 1781(1898)) according to which the influence of an inactive substituent on the rotation decreases with its distance from the asym. complex and that of Frankland and Wharton (*J. Chem. Soc.* **69**, 1320(1896)) according to which the influence of groups on the rotation increases in the order *o*-, *m*- and *p*- when placed in these positions. These amides were in general prepd. by heating a lactone with an amine at a temp. that could be borne without producing decompn. For the methylamides the heating took place in a sealed tube; with the remainder a reflux condenser was used. The products were washed with Et_2O to remove the free amine and then crystd. from EtOH. The rotation was detd. as quickly as possible in aq. soln. in order to avoid sapon. The *methylamide* of arabonic acid (A) seps. as pure white shining crystals, m. 170° (decompn.), $[\alpha]_D^{12}$ 51.1°, $[M]_D^{12}$ 91.4°. The *benzylamide* is colorless, m. 167°, $[\alpha]_D^{10}$ 45.8°, $[M]_D^{10}$ 116.8°. The *ω-phenylethylamide* seps. as voluminous silky needles, m. 173.5°,

$[\alpha]_D^{12}$ 24°, $[M]_D^{12}$ 64.6°. The *ω-p-hydroxyphenylethylamide* seps. as faintly brown crystals, m. 164°, $[\alpha]_D^{15}$ 23.5°, $[M]_D^{15}$ 67.0°. The *β-naphthylamide* gives white crystals, m. 214°, of which the rotatory power in H_2O could not be detd. because of its insoly. in H_2O. α-$C_{10}H_7NH_2$ could not be induced to react with the lactones of **A** up to 175°. The *tetramethylenediamide* of **A** seps. as a heavy white compd., m. 194°, $[\alpha]_D^{13}$ 36.3°, $[M]_D^{13}$ 139.4°. The lactone of **A** with $MeCO_2CH_2NH_2.HCl$(first treated with the calcd. amt. of NaOEt in EtOH for the HCl present) gave *methyl l-arabonylamino acetate*, $CH_2(OH)[CH(OH)]_3CONHCH_2CO_2Me$, m. 124°, $[\alpha]_D^{10}$ 43.3°, $[M]_D^{10}$ 108.7°. The same compds. when MeOH was used as the solvent gave the corresponding *methyl ester* m. 104°, $[\alpha]_D^{16}$ 44.8°, $[M]_D^{16}$ 106.2°, which results are only approx. correct. Attempts to obtain similar derivs. of H_2NCO_2H using urethan and the lactone of **A** gave the unchanged compds. According to Rupe (*C. A.* **4**, 1040) an accumulation of Ph groups causes a strong diminution in the rotatory power (cf. also Ahner, *Trans. Faraday Soc.* **10**, 84(1914), and Chugaev, *C. A.* **7**, 1004). Attempts to test this generalization with the derivs. of Ph_2NH and Ph_3CNH_2 failed because these compds. do not react with the lactone of **A**. Futile attempts to obtain a piperazine deriv. of **A** are described. The *methylamide* of *d*-galactonic acid (**B**) was obtained as a jelly under all conditions and when dry m. 153° (decompn.), $[\alpha]_D^{10}$ 34.5°, $[M]_D^{10}$ 72.1°. The *benzylamide* seps. as nearly white crystals, m. 187°, $[\alpha]_D^{17}$ 55.2°, $[M]_D^{17}$ 157.3°. The *ω-phenylethylamide* seps. as colorless crystals, m. 198°, $[\alpha]_D^{14}$ 21.9°, $[M]_D^{14}$ 65.5°. The α-naphthylamide could not be obtained. The *β-naphthylamide* was obtained in poor yield, m. 214°, of which the rotatory power could not be detd. because of its insoly. in H_2O. The amide of *d*-mannonic acid (**C**) seps. as crystals that m. 175° (Hudson and Komatsu, *C. A.* **13**, 2204, gave 172.3°), $[\alpha]_D^{12}$ −17.2° (Hudson gave −17.3°, $[M]_D^{12}$ −33.5°). The *methylamide* of **C** seps. as short white needles, m. 165.6° (browns), $[\alpha]_D^{12}$ −18.1°, $[M]_{12}$ −37.6°. The *anilide* seps. as colorless crystals, m. 176°, $[\alpha]_D^{12}$ −16.9°, $[M]_D^{12}$ −45.7°. The methylanilide and the *o*-toluidide could not be obtained by this method. The *m-toluidide* seps. as colorless crystals, m. 142°, for which $[M]_D^{12}$ −37.9°, which is not considered to be correct because this compd. is so easily sapond. in H_2O. The *p-toluidide* seps. as slightly colored crystals, m. 179° $[\alpha]_D^{10}$ −18.1, $[M]_D^{10}$ −51.5°. The *benzylamide* seps. as a white compd., m. 164°, $[\alpha]_D^{12}$ −9.1°, $[M]_D^{12}$ −26.1°. The *ω-phenylethylamide* was obtained as a white compd., m. 166°, $[\alpha]_D^{11}$ −7.5°, $[M]_D^{11}$ −22.5°. This amide was most readily prepd. by mixing the lactone and the amine in EtOH and boiling under a condenser. Attempts to prep. amides of *l*-idonic and *l*-xylonic acids by the same method failed. v. W. tried in vain to obtain the α- and β-naphthylamides of **C**. The *methylamide* of *d*-gluconic acid (**D**) was obtained as a powder that m. 127° (decompn.), $[\alpha]_D^{12}$ 33.8°, $[M]_D^{12}$ 70.6°. The *methylanilide* could not be obtained although it is known (Fischer, Passmore, *Ber.* **22**, 2736(1889)). The *o*-toluidide could not be obtained, while the *p*-deriv. was previously obtained by Miss van Marle (*Diss.* 1919, p. 113), m. 181°, $[\alpha]_D^{14}$ 50.9°, $[M]_D^{14}$ 145.1°. The *m-toluidide* seps. as long nearly colorless crystals, m. 158°, $[\alpha]_D^{12}$ 48.7°, $[M]_D^{12}$ 138.8°. The *benzylamide* seps. as colorless crystals, m. 163°, $[\alpha]_D^{12}$ 16.1°, $[M]_D^{12}$ 45.9°. The *ω-phenylethylamide* is a shining colorless compd., m. 151°, $[\alpha]_D^{12}$ 11.1°, $[M]_D^{12}$ 33.2°. The *α-naphthylamide* was obtained in small yield as a colorless compd. m. 178°, $[\alpha]_D^{20}$ 37.9°, $[M]_D^{20}$ 121.7°. The *β-naphthylamide* seps. as rose-tinted crystals, m. 190°, but the rotation could not be detd. in H_2O because of its small soly. Besides the conclusions mentioned at the beginning, the following are given in the summary. The Ph group has a greater influence on the rotation than a Me group. The influence of a Ph group sepd. from the asym. complex by a CH_2 group is comparable to that of an *o*-tolyl group. With *l*-arabonic acid [M] is greater for the benzylamide than for the *o*-toluidide while for *d*-galactonic acid the reverse is true. Comparison of [M] for *o*-, *m*- and *p*-toluidides with that of the anilides shows that

the influence of the *o*-substituted group is least and the *p*- greatest. *p*-$MeC_6H_4NH_2$ reacts easily with the lactones of sugar acids, the *m*-isomer less easily and the *o*-isomer not at all with *d*-mannonic and *d*-gluconic acids. α-$C_{10}H_7NH_2$ reacts with but one of the lactones examd. β-$C_{10}H_7NH_2$ does not readily react with these and the amides formed are so little sol. in H_2O that its influence on [M] could not be detd. These naphthylamides are also difficult to purify so that their importance in the identification of acids of the sugar group will not be great. Ph_2NH, PhNHMe and piperazine react with *l*-arabonic acid lactone with difficulty. The changes produced in the mol. rotation of the compds. examd. by different substitutions are ordinarily accompanied by a change of the m. p. in the same direction. E. J. WITZEMANN

Two new derivatives of α- and β-methyl glucoside (preliminary communication). BURCKHARDT HELFERICH. Univ. Berlin. *Ber.* **54B**, 1082–4(1921).—In the present paper is described a reaction in which the direct replacement of HO groups in glucosides or related compds. by a halogen has, at least in part, been realized. The reaction depends greatly upon the exptl. conditions, other glucoside derivs. containing both Cl and H_2SO_4 residues always being formed. Thus, when 28 g. anhydrous C_5H_5N, 110 cc. $CHCl_3$ and 11.2 g. $SOCl_2$ in ice are treated with 4 g. powdered α-Me glucoside, there begins to sep. after a time a cryst. ppt. (a C_5H_5N compd. which has not yet been investigated) which is filtered off after 2 hrs.; the $CHCl_3$ soln. is washed twice with H_2O, dried with Na_2SO_4, evapd. *in vacuo*, finally at 65°, and the residue (2.4 g.) crystd. from a very little alc. It consists of *α-methyl glucoside dichlorohydrin sulfate*, $C_7H_{16}O_6SCl_2$, needles, $[\alpha]_D^{17}$ 139.97° (AcOH), mol. wt. in freezing $CHBr_3$ 317, m. 104–5°, does not reduce Fehling soln. on short boiling, gives a faint green color on longer boiling, but after heating 0.5 hr. at 100° in 2 *N* HCl sugar can be detected in abundance with Fehling soln. The *β-compound*, similarly prepd. in 0.2 g. yield from 2.5 g. β-Me glucoside, $[\alpha]_D^{17}$ −11.84° (AcOH), m. 137°, gives a faint green color with boiling Fehling soln. unless previously heated a short time at 100° with 2 *N* HCl, when it strongly reduces Fehling soln. CHAS. A. ROUILLER

A new form of galactose methylphenylhydrazone. ÉMILE VOTOCEK. Polytechnic School Prague. *Bull. soc. chim.* **29**, 406–9(1921).—The m. p. of galactose methylphenylhydrazone has varied with different investigators (*Rec. trav. chim.* **15**, 225; *Ber.* **36**, 4373; **37**, 305). V. found that according as it is crystd. from hot 96% EtOH or boiling H_2O, different crystals sep. EtOH yields white scales (**A**) with a pearly luster, m. 190°; H_2O fine silky pale yellow needles (**B**), m. 185–7°. **A** is clinorhombic, with pseudoquadratic character, 0.05–0.1 mm., perfect cleavage on the largest face, irregular contour with n 1.54 and very weak birefringence. **B** is orthorhombic, of rectangular contour, with one or more angles of the parallelograms blunt, the oblique facets cutting irregular angles, a constant angle with respect to the long axis, n greater longitudinally than transversely, a negative bisectrix perpendicular to the largest face, the transverse direction of the largest face corresponding to the max. refraction, the birefringence greater than **A**. There is no stereoisomerism, for **B** is galactose methylphenylhydrazone monohydrate. **B** dried over H_2SO_4 loses 1 H_2O but does not decomp. **A** shows no such loss of H_2O. C. C. DAVIS

Levulosan. AMÉ PICTET AND JOSEPH REILLY. Univ. Geneva. *Helvetica Chim. Acta* **4**, 613–6(1921).—The isolation and analysis of levulosan has been very unsatisfactory (*Compt. rend.* **48**, 1062; *Ann.* **57**, 234(1859); *Monatsh.* **8**, 529(1887); *Ber.* **31**, 68(1898)). Levulose (**A**) was converted to levulosan (**B**) by the method applied by P. and Castan to form glucosan (*Compt. rend.* **14**, 3226). Dried at 100° *in vacuo* a white powder was obtained, with vague cryst. appearance microscopically, m. 150°, very sol. in H_2O and MeOH, slightly sol. in HOAc and C_5H_5N, almost insol. in EtOH, insol. in Et_2O, C_6H_6, Me_2CO, CCl_4, petr. ether and the higher alcs., extremely hygro-

scopic. A 1% soln. has $[\alpha]_D$ 18.6°, a 2% soln. 19.5°. It has a feeble sour-bitter taste. With brewer's yeast at 25° for 6 days there is no fermentation. It does not redden fuchsin decolorized by SO_2, but reduces warm Fehling soln. with exactly 0.33 the activity of levulose. It decolorizes cold neutral $KMnO_4$. Its H_2O soln. changes at 100° to **A**, and after 3 hrs. at 100° in 1% H_2SO_4 soln., neutralized by $BaCO_3$, the soln. has $[\alpha]_D$ −82.5°. **B** heated with N_2H_3Ph in HOAc forms phenylglucosazone, m. 206–7°. **B** in HCl evapd. *in vacuo* gives a cryst. solid, probably levulosyl chloride. **B** in HNO_3 (d. 1.52) at 0°, treated with concd. H_2SO_4, poured into H_2O at 0°, and recrystd. from EtOH, forms the trinitrate, small needles, m. 139–40°. 5 g. of **B** in 40 cc. C_5H_5N and 8 g. MeCOCl let stand several hrs., poured into H_2O and crystd. from dil. EtOH, forms the triacetate, m. 85°. 2 g. of **B**, 15 cc. of C_5H_5N and 5 g. PhCOCl, let stand 1 day, poured into H_2O and crystd. from HOAc, forms the tribenzoate, small rectangular tablets, m. 125–6°, very sol. in cold $CHCl_3$, C_6H_6, Me_2CO and EtOAc, sol. in MeOH, EtOH and CCl_4, slightly sol. in Et_2O, insol. in petr. ether. C. C. Davis

The polyoses of rotted beets. Émile Votocek. Polytech. School of Prague. *Bull. soc. chim.* **29**, 409–13(1921).—A study of 3 samples of gelatinous polyoses previously purified from 96% EtOH. They were gray powders insol. in cold H_2O, swelling in boiling H_2O and without action on Fehling soln. and NH_3-$AgNO_3$ unless previously heated with dil. acids. After hydrolysis the samples gave $[\alpha]_D$ −77.2°, −73.8° and −86.8° with no galactose, pentoses or mannose present. The samples contained 9.5%, 10.9% and 1.4% resp., of glucose, the remainder in each case being fructose. The complex polyoses were fructosans with small amts. of glucosans. C. C. Davis

Inulin. Hans Pringsheim and Alexander Aronowsky. Univ. Berlin. *Ber.* **54B**, 1281–6(1921).—P. has long held the view, and established it experimentally for starch, that ring complexes consisting of several monosaccharide residues held together by secondary valences form the basis of polysaccharides and that in the degradation of the latter two reactions occur side by side: depolymerization without change of the closed cyclic basal substances, and rupture of these basal substances with addition of H_2O which sets free the aldehyde groups and brings out their reducing properties. In the hydrolysis of starch by acids, acetolysis and enzymes a partial depolymerization can be effected but the diminution in size of the mol. of the unchanged basal substance is not sufficient to permit of detg. its mol. wt. by the usual methods, and further depolymerization without at the same time setting free aldehyde groups is impossible. This is even more marked in the case of cellulose and it has thus far been found impossible to diminish the size of the mol. without simultaneously bringing out reducing properties. It has now been found, however, that a non-reducing acetate of inulin can be prepd. whose mol. wt. can be detd. and which on sapon. with alc. KOH regenerates the original inulin. These results, therefore, permit of making a definite mol. wt. detn. of inulin itself, the first complete mol. wt. detn. of a polysaccharide. As starting material were used a com. inulin and a sample prepd. from dahlia bulbs by Dragendorff's method; these, as well as a prepn. from chicory, showed a sp. rotation of not quite −36° and all attempts to free it from by-products by Tanret's $Ba(OH)_2$ method and thus obtain a substance with a rotation of −39.5° failed, as did also all attempts at extn. with 60% alc., in which the by-products are more sol. P. and A. are, therefore, inclined to agree with Dean's criticisms of Tanret's observations (*Am. Chem. J.* **32**, 69(1904)); the by-products are evidently fermentative degradation products of inulin, whose existence in dahlia and Jerusalem artichoke bulbs and chicory roots depends on the season. When 18 g. inulin is heated on the H_2O bath under a reflux with 100 cc. C_5H_5N (distd. over KOH) and 70 cc. Ac_2O reaction sets in in a few min. and continues without further heating until all the inulin dissolves; the soln. is filtered into 1.5 l. cold H_2O allowed to stand overnight, filtered and dried over H_2SO_4 and stick KOH (yield, 27 g.). The product

dissolves easily in 20 cc. AcOH and 60 cc. MeOH but a turbidity soon appears and a cryst. substance begins to sep. on the walls of the vessel (11.2 g. after 2 days); this is completely freed from AcOH by dissolving in 100 cc. boiling MeOH, there being obtained on the next day 10 g. of a now amorphous substance, softens 95°, m. 102–3°, which after recrystn. from 10 cc. of AcOH-MeOH (1:2) and again from MeOH is reduced to 5 g. It contains 49.94% C, 5.62% H, 44.53–44.84% Ac, $[\alpha]_D^{20}$ −42.13° to −42.55° (AcOH), mol. wt. 2624–2635 in freezing $C_{10}H_8$, 2501–2823 in AcOH, 2529–2690 in PhOH, av. 2633. These results correspond to a *triacetylinulin* with 9 sugar residues, $(C_6H_7O_2Ac_3)_9$ (calcd., C 50.00, H 5.62, Ac 44.79, mol. wt. 2593). From 7 g. of the finely powdered acetate rubbed with 7 g. KOH in 100 cc. ice-cold alc., allowed to stand 0.5 hr. at room temp., quickly filtered, washed with alc., taken up in 25 cc. H_2O, neutralized with AcOH, boiled with charcoal and filtered through fuller's earth is obtained a clear soln. from which the original inulin seps. on standing several days. It is identical with the original product not only in its chem. properties and rotation but in the picture which it gives on exposure to Röntgen rays. CHAS. A. ROUILLER

The distillation of methylcellulose under reduced pressure. JOSEPH REILLY. Univ. Geneva. *Helvetica Chim. Acta* **4**, 616–21(1921).—If the atomic grouping of levoglucosan (A) preëxists in the cellulose (B) mol., methylcellulose (C) should form on dry distn. a high % of methyllevoglucosan as B forms A. If not, then the formation of A is not a depolymerization of B but a reaction in which OH groups take part, and cannot take place if the OH groups are alkylated. Woodhouse and Denham (*C. A.* **8**, 243; **9**, 203; **15**, 1693) prepd. a series of products containing 23.6–44.6% of OMe groups by treating B with Me_2SO_4 and NaOH. The mixt. containing 44.6% was almost wholly trimethylcellulose. R. prepd. 4 C mixts. of different OMe content: 25.3% (D), 28.1% (E), 33.4% (F), and 43.7% (G), by the method of Pictet and Sarasin (*C. A.* **12**, 2187) and dry distd each under reduced pressure. Two distillates were collected, one at 60°, the second below 0°. 26 g. of D distd. 0.5 hr. at 10–15 mm. yielded 51% of a paste (60°), 32% of liquid (below 0°), 7% residue, 10% volatile. The paste was sol. in H_2O and EtOH and had 24.3% OMe. Hydrolyzed by dil. H_2SO_4 it reduced Fehling soln., gave a deep red osazone, and had 19.4% OMe. 25 g. of E distd. at 10–15 mm. yielded 51.2% of paste (4 fractions at 60°), 32.5% liquid, 9.4% residue, 6.9% volatile. The first paste fraction was redistd. at 10 mm. and 4 fractions were collected. The distillate with max. OMe had 32.3%, corresponding to dimethyllevoglucosan. This hydrolyzed in 1% H_2SO_4, neutralized and evapd. *in vacuo* yielded a hard, friable mass, corresponding by analysis to dimethylglucose. These results point to the preëxistence of the levoglucosan group in the cellulose mol. F distd. gave similar results to E. 5 g. of G distd. 1.5 hrs. at 1–2 mm. yielded after fractionation a product at 60° with 42.3% OMe (trimethyllevoglucosan 45.6%). The volatile distillate was 6.5 cc. per 1 g. of paste (60°) and contained 43.4% CO_2, 28.9% CO, 0.15% O_2, 3.1% unsatd. hydrocarbons and 23.2% CH_4. C. C. DAVIS

Crystal measurements on benzal-α-acetonaphthone. C. HLAWATSCH. Vienna. *Beitr. Kryst. Min.* **1**, 167–72(1918).—This substance was prepd. by Albrecht (*C. A.* **9**, 911). Optical study showed the crystals to be twins. One n is <1.643, the other >1.658, the double refraction being very strong. The crystal system is triclinic; angular values for 2 different orientations are given. E. T. WHERRY

Some derivatives of *p*-hydroxyphenylglycine. L. GALATIS. Univ. Geneva. *Helvetica Chim. Acta* **4**, 574–9(1921).—Several new derivs. of $HOC_6H_4NHCH_2CO_2H$ (A) are described. 15 g. $HOC_6H_4NH_2Cl$ in 30 cc. H_2O added to 25.2 g. $NaHSO_3$ in 50 cc H_2O treated with 7.5 cc. 40% CH_2O, followed by addition of 7 g. KCN after some hrs., and crystd. at 0°, yields the *compound* $HOC_6H_4NHCH_2CN$, transparent, brilliant massed plates, m. 100° (yield 80%), sol. in EtOH, cold Et_2O and slightly sol. in cold

H_2O. Its H_2O soln. with $FeCl_3$ gives a transient fuchsin-red color. Heated dry it becomes yellow at 160°, red at 190° and decomps. 204° with evolution of NH_3. Boiled with NaOH until no NH_3 escapes and neutralized it yields 65% of A. *Acetyl derivative*, from A and Ac_2O, colorless crystals from EtOH, m. 75°, very sol. in EtOH, Et_2O, C_6H_6, slightly sol. in H_2O and hot petr. ether. *Hydrochloride*, from A in 20% HCl, prisms several cm. long, hydrolyzed by H_2O. *Sulfate*, from A in dil. H_2SO_4, small crystals, hydrolyzed by H_2O. The *compound* $HOC_6H_4N(CH_2CO_2H)(CH_2CN)$, from A and concd. CCl_3CO_2Na boiled 3 hrs., extd. with equal parts Et_2O and EtOH, pptd. with Et_2O, nearly colorless amorphous mass. Equal parts of $ClCH_2CO_2H$, *p*-$HOC_6H_4NH_2$ and NaOH boiled 0.5–1 hr. in 20 parts H_2O, filtered from the A, cooled, filtered, the residue being boiled separately with EtOH until white, recrystd. from H_2O, and treated with an equiv. of HCl, yields the *compound* $HOC_6H_4N(CH_2CO_2H)_2$ (B), small white needles, m. 160° (decompn.), sparingly sol. in cold H_2O, EtOH and Et_2O, very sol. in boiling H_2O and EtOH. It is acid to Me orange and reacts with carbonates and sulfates. Addition of NaOH or Na_2CO_3 gives an intense fuchsin-red, changing to brown, $FeCl_3$ a blue color, and HCl a violet after some secs. *Sodium salt*, small shining white crystals, insol. in EtOH, sparingly sol. in cold H_2O, very sol. in hot H_2O, pptd. from its satd. soln. by NaCl or concd. HCl. *p-Hydroxyaniline salt*, a by-product of the formation of B, extd. by EtOH, crystd. from H_2O, gives a temporary methylene-blue color with excess of $FeCl_3$ and HCl, a yellow with BzH in EtOH, a blood-red with *p*-HOC_6H_4CHO in EtOH, depositing in time blood-red crystals. *Acetyl derivative*, from B in dil. $NaHSO_3$, made alk., shaken with Ac_2O and crystd. from dil. EtOH, white crystals, sparingly sol. in EtOH, very sol. in H_2O. *Hydrochloride*, from 35 g. of $HOC_6H_4N(CH_2CO_2Na)_2$ in 70 g. of hot H_2O and 100 cc. concd. HCl cooled to 0° and filtered (yield 30 g.), hydrolyzed by H_2O. C. C. DAVIS

Conductivity of the arsonic acids (correction). F. FICHTER. Basel. *Ber.* **54B**, 1280(1921).—In the measurements made with Elkind some yrs. ago (*C. A.* **10**, 1038) a considerable error was made in detg. the capacity of the cell so that all the values then published are erroneous; the following are the corrected values for the mol. cond. at 25° for *v* 64, 128, 256, 512 and 1024, resp.: $PhAsO_3H_2$, 46.9, 59.0, 84.9, 110.8, 142 (Λ_∞ 372, av. *K* 0.025). *p*-$H_2NC_6H_4AsO_3H_2$, 21.4, 32.1, 46.4, 65.7, 99.3 (Λ_∞ 370). *o*-$O_2NC_6H_4AsO_3H_2$, 53.2, 71.3, 95.1, 124.5, 157.9 (Λ_∞ 370, av. *K* 0.035). The values for arsanilic acid now agree with those of Lorenz and Schmidt (*C. A.* **15**, 1439), at least for the first dilns. CHAS. A. ROUILLER

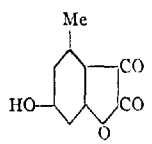
Acetic acid derivatives of *p*-anisidine. J. HALBERKANN. Inst. Schiffs-u. Tropenkrankheiten, Hamburg. *Ber.* **54B**, 1152–67(1921).—*4-Methoxyphenylaminoacetic acid* (*N-p-anisylglycine*) (A), from 20 g. *p*-anisidine (B), 33 g. NaOAc and 4 cc. H_2O heated 0.5 hr. on the H_2O bath with 14.5 g. $ClCH_2CO_2H$, treated with excess of KOH, freed from B with Et_2O, strongly acidified with HCl, freed from the tertiary amine by repeated extn. with Et_2O and neutralized to Congo with KOH, stout needles from AcOEt-benzine, slender tablets from H_2O, m. 154–7° (decompn.), has a fatty feeling, more or less quickly turns yellow to brown in soln. and in the light and on heating to 100°, easily sol. in AcOH (first with a brownish, then a violet color), dil. acids and alkalies, in H_2O with a strong acid reaction, Br turning the soln. blue-violet with strong blue fluorescence changed by NH_4OH to green, gives with $FeCl_3$ a blue-violet color changing to violet-red, reduces $AgNO_3$ with faint mirror formation, the liquid becoming blue-violet, reduces $KMnO_4$ with formation of a red soln., gives white ppts. with $HgNO_3$ and $Hg(NO_3)_2$ which dissolve on heating but reduction follows almost immediately and the soln. becomes blue-violet to red. $HgCl_2$ after long standing produces a yellow cryst. ppt., with slow reduction. Triketohydrindene gives no color. Alk. Br soln. added to A in H_2O produces a play of colors from yellow through green, brown-red, brown to dark

brown-red; if a drop of PhOH has previously been added it changes on the addition of the NaOBr quickly through green and brownish yellow to blue and after long standing, to violet and finally red. Aq. solns. give no color with Co and Ni salts but with a trace of $CuSO_4$ become intensely green, NH_4OH changing the soln. through pink to violet and finally deep violet-blue. *Copper salt*, obtained by boiling solns. of **A** with $CuCO_3$, dull dark green powder of very fine yellow-green needles. *Zinc salt*, stout prismatic needles. *Acetyl derivative* (**C**), from **A** heated some time with 2 mols. Ac_2O, stout whetstone-like needles from alc., m. 185°, easily sol. in alkalies, insol. in dil. acids, gives no color with $FeCl_3$, Br water and NaOBr with or without PhOH, does not reduce Ag, Hg′ or Hg″ nitrate, does not change the color of $CuSO_4$ soln. *Ethyl ester*, from 20 g. **B**, 10 g. $ClCH_2CO_2Et$ and 20 g. AcOEt heated 5 hrs. on the H_2O bath, stout prisms from H_2O, long rectangular plates from alc., thick table-like prisms from ligroin, m. 57–8°, easily sol. in dil. acids, gradually resinifies even over H_2SO_4, gives in H_2O with $FeCl_3$ a red to blue-violet color, behaves like **A** towards Hg′, Hg″ and Ag nitrate and NaOBr; with the latter in the presence of PhOH the soln. becomes only brown-red, not blue; Br water produces only a faint violet color changed to brownish by NH_4OH; $CuSO_4$ soln. is not changed in color; *acetyl derivative*, stable oil easily sol. in the usual org. solvents, gives no color with $FeCl_3$. *Amide*, from the ester and alc. NH_3 at 100°, needles from petr. ether, cholesterol-like tablets or needles from dil. alc., m. 146–7°, easily sol. in dil. acids, gives in aq. alc. with $FeCl_3$ a violet-red color. *Chloroaceto-4-methoxyphenylamide* (**D**), from 20 g. **B** in 150 cc. cold dry C_6H_6 treated dropwise with 9.2 g. $ClCH_2COCl$ and 50 cc. C_6H_6, rectangular leaflets from dil. alc., long needles gradually changing to rhombic needles from abs. alc., m. 121°, gives no color in aq. alc. with $FeCl_3$, produces itching and sneezing. *Triglycolamidic tris-4-methoxyphenylamide*, $(MeOC_6H_4NHCOCH_2)_3N$, from **D** heated 3 hrs. on the H_2O bath with 5 parts NH_4OH, rectangular tablets from alc., m. 295°, insol. in dil. acids and alkalies, gives in alc. with $FeCl_3$ a red color destroyed by H_2O; the alc. mother liquors, treated with H_2O until turbid, yield the *diglycolamidic bisamide*, leaves from H_2O, m. 141°, gives a red color with $FeCl_3$ in alc. and with $CuSO_4$ a green color changed to blue by NaOH. *4-Methoxyphenylaminoacet-4-methoxyanilide*, from equimol. amts. of **B** and **A** heated 2 hrs. at 135°, rectangular leaves from C_6H_6 or H_2O, m. 134°, long flat needles from alc., gives in alc. with $FeCl_3$ after dilu. with H_2O a blue-violet, then dirty violet-red color and a violet-blue fluorescence; Br water or vapors color the substance in aq. suspension green-blue and on heating it dissolves with pink color; in H_2SO_4 (d. 1.48) it gives a deep red color with $FeCl_3$. The same compd. is obtained by heating **D** and 2 mols. **B** 2 hrs. at 120° and finally a short time at 140°; *acetyl derivative*, $MeOC_6H_4NAcCH_2CONHC_6H_4OMe$, from equimol. amts. of **B** and **C** heated about 1 hr. at 175–80°, fine flat needles from 50% alc. or $CHCl_3$-benzine, m. 138°, insol. in dil. acids and alkalies, gives no color with $FeCl_3$. *4-Methoxyphenylbis-4-methoxyphenylaminoacetylamine*, $(MeOC_6H_4NHCH_2CO)_2NC_6H_4OMe$, is formed together with the amide on fusing the components together and remains in the C_6H_6 mother liquor from which, on concn. and addition of a little benzine, it seps. in rhombic leaflets, m. 185°, difficultly sol. in dil. acids, insol. in alkalies, gives in alc. with $FeCl_3$ an olive-brown color changed by H_2O to violet-red (violet-blue in incident light) and in H_2SO_4 a deep red color. With excess of alc. NaOEt (3 mols.) in the cold **D** is completely hydrolyzed in 2 days: with 2 mols. NaOEt the chief reaction is the condensation of 2 mols. **D** to *1,4-bis-4-methoxyphenyl-2,5-diketo-1,4′-diazine hexahydride* (**E**), rhombic leaflets from alc., m. 256°, short needles from $(CH_2Br)_2$, better prepd. by heating **A** for 1 hr. at 155–60° in a current of N. *N-4-Methoxyphenyl-N-[4′-methoxyphenylaminoacetyl]aminoacetic acid*, from 5 g. **E** boiled 3 hrs. with 150 cc. alc. and 15.4 cc. of *N* KOH, freed from most of the alc. by distn. and from the rest by adding 50 cc. H_2O and evapg., treated with 15.4 cc. of *N* HCl and taken up in Et_2O,

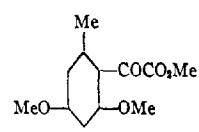
stout or elongated 6-cornered prisms from 60% alc., sinters 110°, loses H_2O, m. turbid 128°, resolidifies and m. again 256°, gives in aq. alc. with $FeCl_3$ a violet color changing to violet-red or red, sol. without color in H_2SO_4; solns. in all org. solvents quickly become brown to red: **E** is easily regenerated, being formed quant. on boiling the C_6H_6 soln.; $FeCl_3$ in H_2SO_4 produces a red color. *4-Methoxyphenylaminoacetomethyl-4'-methoxyphenylamide* (**F**) is obtained in 3 ways: (1) The alc. mother liquor obtained in the prepn. of **E** by heating **A** is shaken some time, after suitably concg., with soda and the undissolved portion with dil. HCl; the latter ext. forms with NaOH a turbidity which is cleared by Et_2O and the Et_2O ext. on evapn. and suitable purification yields a small amt. of stout prismatic columns from alc., m. 118°, easily sol. in dil. acids, insol. in alkalies, easily sol. in H_2SO_4 without color, gives in aq. alc. with $FeCl_3$ a red color quickly changing to blue-violet and gradually to violet-red, in H_2SO_4 (d. 1.84) a deep red color. (2) Equimol. amts. of **A** and *p*-$MeOC_6H_4NHMe$ are heated 3 hrs. at 145–50° and the **F** is extd. from the product (which consists chiefly of **E**) with alc. (3) **F** is obtained in good yield by heating *chloroacetomethyl-4-methoxyphenylamide* 1 hr. at 115° with 2 mols. **B**. The Cl compd. itself is prepd. from $ClCH_2COCl$ and 2 mols. $MeOC_6H_4NHMe$ and seps. from C_6H_6-petr. ether in stout tables, m. 57°, gives no color with $FeCl_3$. *N-4-Methoxyphenyldiglycolamidic acid* (**G**) is formed together with **A** and goes into the Et_2O ext. of the strongly acidified soln. This ext. is shaken with acidified H_2O and then with dil. KOH, with HCl it yields the G_1 stout rectangular columns with 1 H_2O, gradually deliquesces, assuming a pink color, sinters 89°, m. 95–6° with loss of H_2O and m. (anhydrous) 122–3° (decompn.); the soln. in AcOH slowly becomes blue, then violet, that in $CHCl_3$ red, those in other org. solvents brownish, that in H_2O violet; a concd. soln. gives with $FeCl_3$ a red color changing on dilu. through red-violet and violet-blue back to red-violet; Br vapors produce a green to blue fluorescence, the latter being changed back to green by NH_4OH; hot $AgNO_3$, and cold $CuSO_4$ behave in the same way as with **A**; an aq. soln. containing PhOH is gradually colored only a very faint greenish blue by NaOBr; triketohydrindene produces a yellow color in the hot or cold aq. soln. *N-4-Methoxyphenyldiglycolamidic bis-4'-methoxyphenylanilide*, from **G** and 2 mols. **B** heated some time at 170°, very slender, felted, apparently quadrangular needles from C_6H_6, m. 184–5°, gives no color with $FeCl_3$, sol. without color in H_2SO_4; a trace of H_2O_2 or $FeCl_3$ produces a pink color changed by more to a deep greenish blue and on heating through blue and brown to deep red and finally olive-brown. The HCl ext. obtained in the purification of the above compd. yields on addition of NaOH and extn. with Et_2O *[methyl-4-methoxyphenyl]aminoaceto-4'-methoxyphenylanilide*, long quadrangular needles, m. 129–30°, easily sol. in dil. acids, insol. in alkalies, gives in aq. alc. with $FeCl_3$ a crimson color, dissolves in H_2SO_4 (d. 1.84) without color, H_2O_2 producing a green color changed by more of the oxidizing agent into a violet-red to deep blue and, on heating, through violet-blue and red to olive-brown. This compd. is also formed in small amt. by heating **A** and 0.5 mol. **D** at 130°. *N-4-Methoxyphenyldiglycolamidic 4'-methoxyanilide*, $MeOC_6H_4N(CH_2CO_2H)CH_2CONHC_6H_4OMe$, from 2 mols. **A** and 1 mol. **D** heated 1 hr. in an indifferent gas at 130°, then a short time at 140°, tables from 70% alc., sinters 140°, m. 147° (decompn.), easily sol. in alkalies, insol. in dil. acids; the AcOH soln. soon becomes deep blue; $FeCl_3$ in aq. alc. gives a violet-red color, violet-blue in incident light; H_2O_2 colors the H_2SO_4 soln. through pink and deep green to olive-brown while $FeCl_3$ gives a permanent deep blue color changing on heating through red into olive-brown. The compd. is also formed in small amt. from **B** and 0.5 mol. **G** at 170°; if the fusion is effected at 120° this becomes the main reaction; boiled 2 hrs. with 4 parts Ac_2O it gives *1,4-bis-4'-methoxyphenyl-3,5-diketo-1,4-diazine hexahydride*, broad table-like needles on slow, long quadrangular needles on rapid cooling from alc., m. 152°, insol. in alkalies and dil. acids, gives no color with $FeCl_3$, easily

sol. in H_2SO_4 (d. 1.84) with orange-yellow color changed by small amts. of an oxidizing agent (H_2O_2) to a permanent deep red, by larger amts. ($FeCl_3$) through red, red-brown and olive-brown to green. C. A. ROUILLER

Hydroxycarbonyl compounds. V. Products of the reaction of dicyanogen and hydrochloric acid gas on resorcinol and orcinol. P. KARRER AND J. FERLA. *Helvetica Chim. Acta* **4**, 203–12(1921); cf. *C. A.* **14**, 2478.—$(CN)_2$ and HCl react like $(C:NHCl)_2$ on the poly-HO phenols. Thus, when dry $(CN)_2$ and HCl gases are led simultaneously into dry resorcinol in cold abs. Et_2O, *resorcylglyoxylic acid* (**A**) and *2,4,2',4'-tetrahydroxybenzil* (**B**) are the principal products. Other products not identified were formed in minor quantities. **A** crysts. from concd. aq. solns. or from Et_2O-ligroin in long, yellow needles, m. 168°, and gives a brownish red color with $FeCl_3$ in H_2O. K. and F. find **A** identical with the compd. previously synthesized by C. Bülow and H. Wagner (*Ber.* **36**, 1949(1903)), from 2-phenyl-7-hydroxy-1,4-benzopyranol-4-carboxylic acid. B. and W., however, assign it a m. p. of 193°, which the authors believe to be a typographical error. **A** forms an ammonium salt, yellow needles from alc., easily sol. in H_2O, and a *silver salt* (by addition of $AgNO_3$ soln. to the NH_4 salt in H_2O) which crysts. from very dil. solns. as needles and quickly darkens. Attempts to prep. the yoxime, phenylhydrazone and Me derivs. of **A** or to reduce it to the 2,4-dihydroxmandelic acid were unsuccessful. **B**, brownish yellow crystals from dil. alc., m. 256° (decompn.), forms a *phenylhydrazone*, m. 263°, and is transformed into the corresponding *tetramethoxy compound* by the action of Me_2SO_4 in NaOH, large, thick, colorless prisms, m. 125–6° from alc. The action of $(CN)_2$ and HCl on orcinol does not produce the corresponding homologs of **A** and **B** but only the *orcylglyoxylic anhydride* (**I**). This fact is explained as being due to the formation of the intermediate compd., orcyloxalimidyl chloride, whose HCl salt ppts. out quickly as a yellow, cryst. mass, thus preventing the further reaction with another mol. of orcinol necessary to form the diorcyl diketone. The above cryst. mass is extd. with boiling H_2O and the hot aq. soln. cooled. **I** seps. out in orange-yellow needles, m. 212°; it is sol. in hot H_2O but less so than **A**, sol. also in alc. and Et_2O; the aq. soln. is acid to Congo paper. When **I** in dil. NaOH is shaken with Me_2SO_4, *methyl dimethylorcylglyoxylate* (**II**) is obtained, large, colorless needles from dil. alc., m. 73–4°. **II** refluxed with 5% NaOH is hydrolyzed to *dimethyl-*



I



II

orcylglyoxylic acid, m. 138–9° from C_6H_6, readily sol. in alkalies. Mild reduction of the latter (with dil. AcOH and Zn dust at 60°) converts it, surprizingly, not into the expected dihydroxymethylmandelic acid but back to orcinol. A. T. FRASCATI

2,4,6-Trinitroresorcinol (styphnic acid). HANS EINBECK AND LUDWIG JABLONSKI. Lab. d. Verbandes d. Ledertreibriemen-Fabrikanten Deutschlands E. V. *Ber.* **54B**, 1084–9(1921); *Collegium* **1921**, No. 614, 289–93.—When finely powdered and bolted quebracho ext. is added in small portions to 5 parts HNO_3 (d. 1.4) in a large beaker in H_2O at such a rate that the mixt. does not foam over and is then cautiously warmed on the H_2O bath and finally concd. to crystn. and the product, in 20 parts H_2O, is made faintly alk. with NH_3, then faintly acidified with AcOH, treated hot with excess of $CaCl_2$, filtered from the $(CO_2)_2Ca$ and evapd. *in vacuo* to incipient crystn. and the resulting Ca salt in 10 parts H_2O is treated with a slight excess of dil. HCl there seps. styphnic acid,

stout faintly yellow prisms from 10 parts alc., m. 179–80°, stout prisms and long lamellas with solvent of crystn. from 5 parts AcOH. As none of the methods for the identification of this acid given in the literature is satisfactory, E. and J. applied to it the Perkin method of pptg. alc. tannin and phenol solns. with alc. KOAc. When the soln. of the acid in 30 parts alc. is treated dropwise with 20% alc. KOAc the orange flocculent ppt. of the di-K salt first formed goes over on rubbing with a glass rod into the light yellow cryst. mono-K salt. When the orange ppt. no longer changes into the light yellow product, it is filtered off, washed with alc. and dried at 100°; the *monopotassium styphnate* seps. from 10 parts H_2O in light yellow prisms with 1 H_2O, explodes violently on a Pt foil. The *dipotassium salt* seps. from 10 parts H_2O in moss-like bundles of orange needles and also explodes violently. *Monosodium salt*, needles with 3 H_2O, losing 1 mol. at 100°, explodes violently 120–30°; *disodium salt*, seps. from H_2O as a light yellow cryst. magma which rearranges into cauliflower-like aggregates of granules, explodes violently on Pt foil, loses 3 H_2O at 130°. CHAS. A. ROUILLER

Condensation of 2,4,6-trinitrophenylhydrazine with quinones. W. BORSCHE. Univ. Göttingen. *Ber.* **54B**, 1287–90(1921); cf. *C. A.* **2**, 854.—It has now been found that under the proper conditions 2,4,6-$(O_2N)_3C_6H_2NHNH_2$ (**A**) can also be made to condense readily with quinones to trinitrohydroxyazo compds. The failure to obtain these compds. before was probably due to their unexpectedly great sensitiveness, being rapidly decompd. into N, picric acid and the corresponding phenol by dil. alkalies at room temp. *2,4,6-Trinitro-4'-hydroxyazobenzene* (4.9 g. from 4.88 g. **A** in 400 cc. hot alc. and 40 cc. fuming HCl treated with 2.16 g. *p*-O:C_6H_4:O in 65 cc. alc., then with 360 cc. H_2O, and allowed to stand overnight), dark red needles with blue shimmer from AcOH-H_2O (3 parts of 30% AcOH to 10 parts H_2O), m. 194–5°, sol. in KOH or NH_4OH with purple, in concd. H_2SO_4 with orange-red color, repptd. unchanged from the latter when poured into ice H_2O; the alk. soln. quickly changes to a dirty brown, foams and on acidification yields a flocculent brown ppt. consisting chiefly of picric acid and PhOH; *benzoate*, long flat orange-red needles from AcOH, m. 191°. *3'-Methyl-2,4,6-trinitro-4'-hydroxyazobenzene*, from toluquinone, garnet-red tablets with 1 H_2O from AcOH-H_2O (4:1), m. 196°, sol. in dil. NaOH with blue-red, in concd. H_2SO_4 with orange-red color. Thymoquinone does not react so readily and under the above conditions a part of it remains unchanged; the filtrate on spontaneous evapn. yields orange-red iridescent leaflets m., after crystn. from dil. alc., 142–4° (decompn.), having the compn. $C_{22}H_{21}O_{13}N_{10}Cl$ (1 mol. of the azo compd. + 1 mol. **A** + 1 mol. HCl), but the AcOH soln. on cautious diln. yields the *2'-methyl-5'-isopropyl-2,4,6-trinitro-4'-hydroxyazobenzene* in yellow-red leaflets, m. 162–3°, sol. in NaOH with violet, in H_2SO_4 with orange-red color; yield, 1.2 g. from 1.64 g. thymoquinone. *4-[2',4',6'-Trinitrobenzeneazo]-1-naphthol*, from α-naphthoquinone, dark red crystals with blue shimmer from AcOH, m. 249° (decompn.), sol. in NaOH with blue-violet, in H_2SO_4 with purple color. *2-Azo isomer*, from β-naphthoquinone, brown needles from AcOH, m. 230° (decompn.), sol. in NaOH with violet, in H_2SO_4 with olive-green color. *4,4'-Bis-[2'',4'',6''-trinitrobenzeazo]azoxybenzene*, dull brown needles, deflagrates 321°, is obtained in 0.6 g. yield when it is attempted to decomp. with boiling AcOH the *compound*, red-brown cryst. flocks, decomp. 165–6°, which is formed in 1.25 g. yield from 2.44 g. **A** and 1.25 g. *p*-O:C_6H_4:NOH. C. A. R.

The reagent "iodine and alkali." Action upon some organic nitrogen compounds. PAUL ROBIN. *Ann. chim.* **16**, 77–140(1921).—In an aq. soln. of "I and alkali" (**A**) the reactions taking place are (*1*) 2 I + 2 NaOH $\rightleftharpoons$ NaI + NaOI + H_2O, and (*2*) 3 NaOI = 2 NaI + $NaIO_3$ (cf. Bougault, *J. Pharm. Chim.* [7] **16**, 33). When a substance capable of reacting with NaOI is introduced there are 2 possible reactions, namely, (*3*) RH + IONa = RI + NaOH, and (*4*) RH + IONa = ROH + NaI.

The extent to which (3) or (4) proceeds is dependent on the ratio of their velocity to that of (2). The degree of alkalinity governs very largely the oxidizing potential. R. has studied the action of A upon the oximes, amidoximes, hydramides, and amidines of some aromatic aldehydes and nitriles. I. **Action upon the oximes.** R. has found that *benzaldoxime, anisaldoxime, piperonaldoxime, and cinnamaldoxime* gave with A the corresponding *peroxides* in good yields. On the other hand the oximes of the extra-nuclear aldehydes, as phenylethylic, phenylpropylic, etc., did not give peroxides but were converted back to the aldehydes. Various *ketoximes, camphoroxime, acetophenone oxime*, etc., were not attacked at all by A. It appears that formation of the peroxides is dependent upon the strongly electronegative groups attached directly to the aldehyde groups. The reaction was carried out by agitating a C_6H_6 soln. of the oxime with aq. Na_2CO_3 and gradually adding a soln. of I in aq. KI. The product always crystd. out. PhCH:NOH (B) gave in this way 35% of the theory of the corresponding peroxide, $(PhCHNO)_2$ (C), m. 110° (decompn.). BzOH and HNO_2 were identified in the aq. soln. while 6% benzoylbenzaldoxime (D) and 20% dibenzenyloxoazoxime (E) were found in the C_6H_6 layer. R. has studied the decompn. of C by A and found it to yield E, BzOH, and HNO_2, thus throwing light on the course of the action of A on B above. The decompn. of C in boiling C_6H_6 gave only B and E. On long standing C decomps. into B, dibenzenylazoxime, a reduction product of E, and nitrobenzene derivs. Anisaldoxime (F) gave with A an 85% yield of the corresponding peroxide $(MeOC_6H_4CHNO)_2$ (G), m. 119° (decompn.), the latter being much more stable than C. G decomps. in boiling C_6H_6 essentially like C. The decompn. depends primarily on the simultaneous reduction of part of G to F and oxidation of part to *dianisenyloxoazoxime* (H). When G is decompd. by A there is no F formed, the oxidation being taken care of by the A, the products being otherwise the same. B crystd. in white silky needles, turning pale yellow in the air, m. 182° (decompn.), is very sol. in HOAc and in Me_2CO, but only slightly sol. in C_6H_6 or Et_2O, is an oxidizing agent like E, but gives no I addition compd. *Dianisenylazoxime* is a very stable compd. obtained by the reduction of H by Zn + HOAc, sol. in C_6H_6 but only slightly sol. in HOAc, Me_2CO, and Et_2O, m. 135° (decompn.). Piperonaldoxime (J) gave with A 85% of the corresponding peroxide (K) m. 134° (decompn.), more stable than either C or G, practically untouched by A and its decompn. in boiling C_6H_6 was more difficult, giving among other things *dipiperonenyloxoazoxime* (L), and its reduction product *dipiperonenylazoxime* (M). L is obtained in clear brown crystals almost insol. in all usual solvents except HOAc in which it is about 3% sol., m. 190° (decompn.), resists hydrolysis much more than either E or H, but does give some piperonic acid. M is a very stable compd. almost insol. in all the usual solvents, m. 208° without decompn. Cinnamaldoxime yields with A 45% of the corresponding peroxide $(PhCH=CHCHNO)_2$, m. 119° (decompn.), rapidly decompd. in boiling C_6H_6. *o*-Nitrobenzaldoxime gave with A similarly the corresponding peroxide, $(NO_2C_6H_4CHNO)_2$, m. 117° (decompn.), likewise decompd. by boiling C_6H_6. II. **Action upon the amidoximes.** The action of A upon the amidoximes is very different with the use of NaOH from its action with the use of Na_2CO_3. In the presence of NaOH the amidoximes are oxidized to the corresponding nitriles. In the presence of Na_2CO_3 or $NaHCO_3$ benzenylamidoxime gives easily benzenylhydrazoximaminobenzylidene, m. 130°. Under similar conditions piperonenyl- and anisenylamidoximes gave practically no reaction. On the other hand phenylacetenylamidoxime is oxidized even by I and Na_2CO_3 rapidly to $PhCH_2CN$. III. **Action upon the hydramides.** The action of A, using Na_2CO_3, upon hydrobenzamide, hydroanisamide, and hydropiperonamide, gives by a complex oxidation the corresponding cyaphenins in 30–40% yield along with some of the corresponding aldehyde, *e. g.*, BzH, etc. The mode of formation is indicated. R. has shown that cyaphenin yields upon hydrolysis with HOAc and HCl, a mixture of

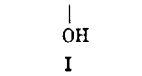
benzamidine, BzOH and NH_3. The anisyl and piperonyl derivs. acted similarly to the above. IV. **Action upon the amidines. Iodoamidines.** See Bougault and R., *C. A.* **15**, 1703. OREGON B. HELFRICH

Tannins and similar compounds. VII. Stereoisomeric catechols. KARL FREUDENBERG, OTTO BÖHME AND ALFRED BECKENDORF. Univ. Kiel u. Bay. Akad. Wiss., München. *Ber.* **54B**, 1204-13(1921); cf. *C. A.* **15**, 846.—While Perkin's "Kath" yields 20–5% cryst. aca-catechol (*J. Chem. Soc.* **87**, 398(1905)) com. Pegu catechu gives only 6%; 20 g. of the ground catechu is rubbed with 10 cc. Me_2CO, treated with 100 cc. Et_2O, decanted after a few min., the sediment being treated again in the same way, dild. to 300 cc. with Et_2O, filtered, concd., treated with 50 cc. H_2O concd. *in vacuo*, made up to 100 cc., treated with a little neutral $Pb(OAc)_2$, freed from Pb with H_2S, concd. *in vacuo* and allowed to stand 24 hrs.; 4 g. of the air-dried product in 25 cc. alc. and 10 cc. Me_2SO_4 treated with gentle warming in the course of 3 min. with 20 cc. of 50% KOH, then dild. with 400 cc. H_2O, yields 4 g. of crude tetramethyl-aca-catechol, which on reduction and methylation by Kostanecki and Lampe's method yields 2,4,6,3′,4′-pentamethoxy-α,γ-diphenylpropane, identical with the product obtained from Gambir-catechol, confirming the suggestion already made that the two catechols are stereoisomeric; the propane obtained from either source seps. in monoclinic prismatic crystals, $a:b:c = 0.7599:1:0.7735$, β 93°57′, *b*(010), *m*(110), *p*(101), *s*(102). From 5 g. air-dried Gambir-catechol (purified with $Pb(OAc)_2$) in 20 cc. C_5H_5N allowed to stand 2 hrs. with 25 cc. Ac_2O and decompd. with ice is obtained 6 g. crude pentaacetyl-catechol, m. 132° after crystn. from 30–40 cc. 96% alc. containing a few drops of AcOH, $[\alpha]_D^{17}$ 40.6° in $(CHCl_2)_2$, these consts. not changing on further crystn. The acetylation of aca-catechol proceeds similarly, but the yield is not so good; after repeated crystn. from alc. the product m. very indefinitely around 156° and shows a rotation in 10% $(CHCl_2)_2$ soln. of −11° to −13°; a sample repeatedly crystd. from $CHCl_3$-MeOH finally gave a rotation of 0° and m. 165°; the crude product, mixed with ⅓ part of that obtained from Gambir-catechol, yields an inactive mixt. m. very indefinitely around 150°, which on one recrystn. from alc. is quant. converted into the inactive compd., m. 165°, which must therefore be a racemate and is also obtained by acetylation of *dl*-catechol (see below). When 5 g. Gambir-catechol are boiled 8 hrs. at 100–3° in 50–100 parts NaCl soln., extd. 18 hrs. with Et_2O and crystd. from a little H_2O there is obtained 2.5 g. of a cryst. mixt. of *d*- and *dl*-catechols for on acetylation it yields, besides the *d*-penta-Ac compd., a large fraction with smaller rotation (14°). Similarly from 2 g. Gambir-catechol in 8 cc. C_5H_5N allowed to stand 3 hrs. at 20° with 8 cc. BzCl is obtained a good yield of a pentabenzoylcatechol, stout needles from Me_2CO-EtOH (2:1), m. 170–2°, $[\alpha]_D^{18}$ 55.4° in $(CHCl_2)_2$, while aca-catechol yields a product m. indefinitely about 177–9°, with a rotation of −13°. The following values for $[\alpha]_D^{17-8}$ for the free Gambir-catechol in 9% soln. in various solvents were found: −0.47° (96% alc.), 3.7° (50% alc.), 11.0° (com. Me_2CO), 18.4° (0.9% soln. in H_2O). The authors conclude that the Gambir-catechol is the almost pure *d*-form while aca-catechol is a mixt. of the *d*- and *l*-forms, with the *l*-form prevailing. CHAS. A. ROUILLER

Derivatives of some *o*-nitroketones. S. GABRIEL AND WILH. GERHARD. Univ. Berlin. *Ber.* **54B**, 1067–78(1921).—If in the prepn. of *o*-$O_2NC_6H_4COMe$ from $O_2NC_6H_4COCH(CO_2Et)_2$ (Gevekoht, *Beilstein* (3rd ed.) **3**, 122) a pure ester, purified through the K salt, is used the resulting ketone solidifies on cooling and seps. from 0.5 part alc. in crystals m. 28–9° (yield, 70%); treated in hot AcOH with Br until the color persists, it yields *ω-dibromo-o-nitroacetophenone*, rhombic tables and leaflets from alc., m. 84–5°. *ω-Phthalimido-o-nitroacetophenone*, from 15 g. $O_2NC_6H_4COCH_2Br$ in 60 cc. Me_2CO slowly treated with 12 g. $C_6H_4(CO)_2NK$ and boiled 1 hr. under a reflux, needles from AcOH, m. 104–5°; 1 g. in 10 cc. hot AcOH treated with 2.5 g. crystd.

$SnCl_2$ in 3 cc. fuming HCl and then with 25 cc. hot H_2O gives the *o-amino compound*, lemon-yellow rhombohedrons or rhombic tables, m. 201–2°, dissolves momentarily in concd. HCl but soon seps. as the *hydrochloride*, rhombic crystals, m. 240–1°, sol. in a little H_2O and reconverted into the free base by more H_2O. When 2.5 g. of the base is boiled 1.5 hrs. under a reflux with 25 cc. concd. HCl, cooled, filtered and evapd. and the resulting HCl salt is crystd. from alc. and treated in H_2O with NH_4OH, there is obtained *ω,o-diaminoacetophenone*, NH_4Cl-like crystals, gradually becomes pink in the air and deep violet on the H_2O bath or *in vacuo* at 100° and begins to m. 123–8°; *dihydrochloride*, microneedles with 2 H_2O from AcOH, m. 197–8° (foaming). Pure *o*-$O_2NC_6H_4COCH_2CO_2Et$ (A) (Needham and Perkin, *J. Chem. Soc.* **85**, 148–55) is obtained in the form of needles from alc., m. 35–6°, from 26 g. of the K salt of $O_2NC_6H_4COCHAcCO_2Et$ (crystd. from 13 parts alc.), 13 g. NH_4Cl, 200 cc. H_2O and 20 cc. NH_4OH almost completely evapd. on the H_2O bath, treated with H_2O, extd. with Et_2O and dissolved out with dil. KOH; addition of more KOH ppts. the *potassium salt* of A as a yellow cryst. magma sepg. from alc. in fine yellow needles (8.5 g.), forming a strongly alk. aq. soln. from which CO_2 ppts. out the free A. A is also formed in the incomplete hydrolysis of $O_2NC_6H_4COCH(CO_2Et)_2$ with alkalies and by esterification of the free $O_2NC_6H_4COCH_2CO_2H$ (B) with HCl and alc.; B is also formed when 10 g. $O_2NC_6H_4COCH(CO_2Et)_2$ is heated 10 min. on the H_2O bath with 20 cc. concd. H_2SO_4 and poured upon ice; distd. *in vacuo*, it decomps. smoothly into CO_2 and $O_2NC_6H_4COMe$. B and 6 mols. $FeSO_4$ satd. with NH_3 and warmed, filtered and treated with AcOH yield 2,4-dihydroxyquinoline. Br and B in C_6H_6 yield *o-nitrobenzoylbromoacetic acid*, cryst. powder, m. 94–5° (foaming), in the powdered form violently irritates the mucous membranes. When 10 g. of the K salt of A is boiled under a reflux in 50 cc. Me_2CO with 5 cc. MeI until the yellow color disappears and the soln. is evapd. there results a sirup almost completely sol. in KOH and giving with excess of alkali a red-yellow oil, probably the K salt of the expected *ethyl α-o-nitrobenzoylpropionate* (9 g.) which, gradually added to 36 cc. hot HI and treated with PH_4I to remove the resulting brown color, gives 7.5 g. of *3-methyl-2,4-dihydroxyquinoline*, needles from H_2O, does not m. 270°, sol. in alkalies, NH_4OH and hot soda, repptd. by acids and yields with HCl a salt hydrolyzed by H_2O; 1.5 g. heated with 2 g. PCl_5, poured into H_2O and distd. with steam give *3-methyl-2,4-dichloroquinoline*, m. 83–4°. If $O_2NC_6H_4COCHAcCO_2Et$ or its Na salt (4 g.) is boiled 45 min. under a reflux with 16 cc. HI (b. 127°) and 1.5 g. red P and the resulting cryst. mass is spread on clay and treated with boiling H_2O, there dissolves an HI salt giving with NaOAc 4-hydroxyquinaldine; the portion insol. in the H_2O on extn. with hot soda and pptn. with AcOH yields 2,4-dihydroxyquinoline. The original ester therefore partly loses the CO_2Et and partly the Ac group and it might be expected that there would be formed as intermediate products $O_2NC_6H_4COCH_2Ac$ (C) and A, resp. When, however, 3 g. preformed C is gradually added to 12 cc. hot HI and 1 g. red P and boiled 10 min. it gives, not 4-hydroxyquinaldine but a *compound* $C_{10}H_9O_2N$ with 1 atom more of O, pptd. from dil. NH_4OH by AcOH in microrodlets, m. 247–8° (foaming), sol. in boiling H_2O and alc. only in traces, sol. in about 25 parts boiling 50% AcOH, easily in NH_4OH and alkalies, gradually becomes reddish to bluish in the air, does not reduce Fehling soln.; *hydrochloride*, pptd. by excess of HCl, fine needles with 1 H_2O, sol. in a little H_2O and then deposits the free base which redissolves on addition of a little HCl; *chloroplatinate*, flat needles and rhoms; *hydroiodide*, crystals with 1 H_2O. The base is obtained in even better yield (11 g.) by adding 20 g. C in small portions to 50 g. crystd. $SnCl_2$ in 100 cc. fuming HCl (keeping the temp. at 65–70°), dissolving the resulting cryst. magma in hot H_2O, satg. with NH_3, filtering and pptg. with dil. AcOH. Apparently in the reduction there is first formed the compd. $HONHC_6H_4COCH_2Ac$, which by loss of H_2O and ring formation gives a compd. I or II (or III);

which of these formulas is correct cannot yet be stated definitely; provisionally the latter is given the preference and the new base is designated as *4-hydroxyquinaldine oxide*. That it is closely related to 4-hydroxyquinaldine is shown by the fact that it is converted into the latter by heating with HI and red P at 200° and that on boiling with PCl_3 it gives 4-chloroquinaldine which, in the form m. 42–3°, contains 1 H_2O. The new base with excess of KOH gives a gelatinous ppt. but with excess of NaOH forms a *sodium salt*, scaly leaves with 7 H_2O, which when heated with Me_2SO_4 dissolves and on concn. yields a cryst. crust leaving Na_2SO_4 undissolved when extd. with alc.; addition of Et_2O to the alc. ext. ppts. fine needles of the quaternary *acid sulfate* **IV**; *picrate*, needles from alc., m. 194°; *chloride*, from **IV** and $BaCl_2$, ppt. from alc. by Et_2O, is intensely bitter and gives with KOH a currant-red oil no longer completely sol. in H_2O; *nitrate*, needles with 1 H_2O. *Picrate* of **II**, needles from alc., m. 171°. *Benzoyl derivative*, from **II** in alkali and BzCl, granules and leaves from 50% AcOH, m. 236–7°; *methiodide*, from the components in Me_2CO at 100°, m. 130°; *picrate*, silky needles, m. 204–5°. If 1.5 g. **II** in 30 cc. hot AcOH is treated with 2 cc. HNO_3 (d. 1.2), it yields 3-nitro-4-hydroxyquinaldine, m. above 280°, but if 11 g. **II** in 130 cc. H_2O and dil. H_2SO_4 is treated cold with 25 cc. concd. HNO_3 the whole mass suddenly turns at 40–50° into a yellow cryst. magma (9 g.) of *4-hydroxy-3-nitroquinaldine oxide* (**D**), decomps. about 227°, dissolves in aq. alc. NaOH with orange-red color and on cooling seps. in brick-red needles which become orange-yellow at 100°, probably with loss of H_2O, and then have the compn. $C_{10}H_7O_4N_2Na$. If the red salt is heated with acid-free Me_2SO_4 it yields the *methyl ether*, $C_{10}H_7O_4N_2Me$, light yellow needles from much H_2O or from 50% AcOH, m. 192°. When 5 g. **D** is added in small portions to 200 cc. hot HI and 2 g. red P, boiled 13 min. under a reflux, decolorized with PH_4I, filtered after several hrs., spread on clay, dissolved in H_2O containing a little SO_2, filtered and treated with NaOAc or with $KHCO_3$ to faintly acid reaction there is ppt. a *basic hydroiodide*, $3C_{10}H_{10}ON_2.2HI$, needles and leaflets, m. about 220°, of 3-amino-4-hydroxyquinaldine, needles with 0.5 H_2O, turning yellow at 100° or *in vacuo* over H_2SO_4 and m. (anhydrous) 258°, gives with Ac_2O an *acetyl derivative*, rodlets insol. in NH_4OH and dil. HCl, sol. in KOH, volatilizes before melting. From 2 g. **D** shaken with 8 g. $SnCl_2$ in 16 cc. fuming HCl, filtered after 1 hr., taken up in H_2O, treated with excess of NH_3, shaken at 50–60° with charcoal and faintly acidified with AcOH is obtained *4-hydroxy-3-aminoquinaldine oxide*, lemon-yellow leaflets and needles, darkens about 240°, m. 258°, sol. in acids, alkalies and NH_4OH; *hydroiodide*, yellowish needles with 2 H_2O; *hydrochloride*, reddens 212°, blackens at higher temps.



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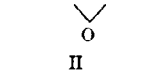

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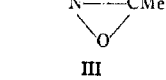


III

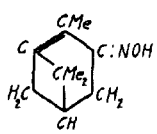
CHAS. A. ROUILLER

A method of preparation of ethyl succinylsuccinate. M. SOMMELET AND P. COUROUX. Faculty of Pharmacy, Paris. *Bull. soc. chim.* **29**, 402–6(1921).—$ClCH_2COCH_2CO_2Et$ (**A**) reacts with EtONa or PhONa like the corresponding Br compd. (*Ann.* **219**, 94; **245**, 74; *Ber.* **29**, 1045). 16.5 g. of **A** added slowly to 2.3 g. of Na in 40 cc. abs. EtOH, heated 1 hr. at 100°, evapd., extd. with H_2O to remove NaCl, air-dried, washed with Et_2O till yellow, dried and crystd. from EtOH, yields 3.7 g. of the cyclic compd.

$CH_2.CO.CH.CO_2Et$
$EtO_2C.CH.CO.CH_2$ (**B**), clear yellow plates or needles, m. 125–6°, sol. with yellow color

and blue fluorescence in hot EtOH, gives a red-violet color with $FeCl_3$ and yellow in NaOH. 82 g. of **A** added to 500 cc. of *N* PhONa while cold, shaken 4 hrs., the insol. compd. being air-dried, washed with EtOH and crystd. from EtOH, yields 36 g. of **B**, very pale yellow plates, m. 126–7°. C. C. DAVIS

Chemistry of pinene. III. Constitution of nitrosopinene and its transformation products. L. RUZICKA AND H. TREBLER. *Helvetica Chim. Acta* **4**, 556–74(1921); cf. *C. A.* **15**, 13.—Ketones and alcs. of compds. in the pinene (**A**) series, though rare in nature, are easily accessible through certain transformations of **A** and for the transformation of **A** into O derivs. nitrosopinene (**B**) is of importance. Wallach (*C. A.* **6**, 2079) proposed for **B** the formula **I** on the grounds that HCl is split out in the same way as in the case of the monocyclic nitrosochlorides where isonitroso compds. result with a double bond in the ring. Bredt showed that in the camphor series a C atom which is common to 2 rings and also bears a double bond cannot exist. R. and T. sought to show the position of the double bond. Pinylamine (**C**), formed by the reduction of **B** with Zn and AcOH, gives with HNO_2 pinocarveol (**D**) and this with CrO_3 gives pinocarvone (**E**), the oxime (**F**) of which differs from **B** and the reduction of this oxime gives an amine (**G**) which differs from **C**. The constitutions of **D**, **E**, **F**, and **G** have been proved by Wallach (pinic acid (**H**), from **D** and **E**.) The oxidation of **B** and **C** with $KMnO_4$ gave no deriv. suitable for proving the constitution, at least no **H** was formed. Earlier work showed the superiority of O_3 over $KMnO_4$ in the case of the semicyclic double compds., and R. and T. ozonized **B**. 10 g. **B** prepd. according to Wallach's method (*Ann.* **346**, 233(1906)), m. 130° from EtOAc, in 200 cc. CCl_4 were exhaustively ozonized; a small amt. of an insol. ozonide sepd. The mixt. after standing 15 hrs. was refluxed for 2 hrs., the solvent was removed and the water was also removed (*in vacuo*) and in the condensate CH_2O and HCO_2H were present. Dimethyldihydroresorcinol gave bisdimethyldihydroresorcinol, m. 187°. The residue from the distn. was taken up in ether, shaken with soda and on acidifying an amorphous acid product of unknown compn. was obtained. The ether contained 6 g. of a yellow neutral product which yielded isonitrosonopinone semicarbazone, crystals from EtOAc, m. 220° (decompn.). 4.5 g. acetylpinylamine (**J**) prepd. according to Wallach's method (*Ann.* **268**, 203(1892); **346**, 241(1906)) in 50 cc. glacial AcOH were ozonized, part of the ozonide sepg. The mixt. was heated 2 hrs. on the water bath, the solvent was evapd. *in vacuo* at 30° and the yellow residue was shaken with ether and soda. A neutral product (1.5 g.), insol. in soda, solidified on standing several days, and acetyl-α-aminonopinone, crystals from C_6H_6 and petr. ether, m. 120–1°, were formed. 4.5 g. **J** in 50 cc. CCl_4 were ozonized and after H_2O was added the mixt. was heated under a reflux for 2 hrs. and the CCl_4 was distd. The oxidation product insol. in H_2O was sepd. with ether, and CH_2O and HCO_2H were found. The splitting out of CH_2O and isonitrosonopinone confirms Bredt's views, and the structure of nitrosopinene is represented by the formula **II**. In ozonizing pinylamine unstable aminoketones must result and with a protected NH_2 group as in the Ac deriv. acetylaminonopinone was formed H. E. W.



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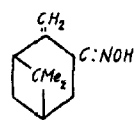
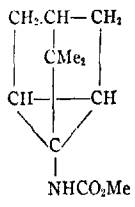


II

Apotricyclol, a derivative of cyclopropanol, and its ketonization. P. LIPP AND C. PADBERG. Techn. Hochschule Aachen. *Ber.* **54B**, 1316–29(1921); cf. *C. A.* **14**, 3237; Meerwein and van Emster, *C. A.* **15**, 854.—Tricyclenic amide (1 g.) in 2 parts cold abs. MeOH is treated with 0.28 g. Na in 6–7 g. MeOH and then dropwise with 0.93 g. Br, boiled 1 hr. under a reflux, freed from the MeOH, and taken up in H_2O and Et_2O (generally a small amt. of a cryst. meal remains undissolved between the two

layers; see below); the aq. faintly alk. soln. contains a small amt. of tricyclenic acid, while the Et_2O soln. yields, besides a little of the unchanged amide, 75% of *methyl apotricyclylurethan* (I), $b_{15.5}$ 128–42°, prisms from petr. ether, m. 85.5–6.0°. The insol. cryst. meal (see above) is *tricycloylapotricyclylurea*, $C_9H_{13}NHCONHCOC_9H_{13}$, needles from xylene, decomps. 238–9°. When 4 g. crude I is boiled 1 hr. under a reflux with 20 cc. of 40% H_2SO_4 CO_2 is evolved and steam distn. of the residue yields 2 g. camphenilone (A), b_{15} 74–7°. Boiling concd. KOH in H_2O or MeOH has practically no effect on I but when 5 g. of the I is fused with 10 g. powdered KOH, heated 5 min. at 160°, taken up in a little H_2O and distd. with steam into dil. HCl, the distillate then being evapd. to dryness *in vacuo* at the lowest possible temp., there is obtained 4.1 g. of the *hydrochloride*, non-hygroscopic cryst. scales, of *apotricyclylamine*, $C_9H_{13}NH_2$, which sublimes *in vacuo*, b. 176.8–7.0° in H, solidifies to a paraffin-like mass m. about 104°, has the typical penetrating amine odor, evolves NH_3 after some days in the air and gradually changes into a viscous yellowish oil. The reaction, however, does not stop completely with the formation of the amine. Under the above conditions only a small amt. of a N-free product, m. 64–6°, is obtained when the HCl soln. of the product is concd. but if during the fusion with KOH the temp. is raised to 180–200° for about 15 min. its amt. increases and by boiling 3 hrs. with an excess of $H_2NCONHNH_2$ and distg. with steam it can be sepd. into A, which remains behind as the semicarbazone, m. 226–7°, and camphenilol (B), b_{748} 199–200°, m. 78–9°, identified through its phenylurethan, m. 100–2°, and by its oxidation to A with CrO_3 in 50% AcOH; finally, the alk. sapon. liquid contains HCO_2K, identified by its reaction with $HgCl_2$ after acidifying and distg. The MeOH set free in the hydrolysis of I reduces, as MeOK, the A to B and is itself oxidized to HCO_2H. The *sulfate* of the amine is well crystd.; *chloroplatinate*, prismatic orange-yellow crystals; *picrate*, yellow prismatic crystals from alc., m. about 200° (decompn.); *phenylurea*, from the amine and PhNCO in Et_2O, needles, m. 222°. When the amine and $COCl_2$ are brought together in Et_2O the HCl salt of the amine is at once pptd. and the Et_2O, after washing with H_2O, leaves a faintly colored oil of penetrating odor, probably *apotricyclyl isocyanate*, which on gentle warming with dil. NaOH yields *sym-diapotricyclylurea*, asbestos-like felted needles from PhMe, decomps. 243°, while with $PhNH_2$ in the cold is obtained the above phenylurea. *Monoapotricyclylurea*, from 1 g. of the amine-HCl and 0.48 g. KNCO, each in concd. aq. soln., brought together in the cold, then boiled a short time, needles from AcOEt-petr. ether, m. 173–4°. *Benzoylapotricyclylamine*, prismatic crystals from aq. alc., m. 173°. *Acetyl derivative*, from the amine and Ac_2O in Et_2O, flat prisms from dil. alc., m. 177°, has an unusual power to sublime. When the amine-HCl in cold concd. soln. is treated with 1.5 mols. $NaNO_2$ the *nitrite* seps. as a sandy ppt., which, however, easily redissolves on gentle warming; on distg. with steam, extg. the distillate with Et_2O and repeatedly washing the ext. with dil. acid and H_2O, *apotricyclol*, $C_9H_{13}OH$, is obtained in 50–5% yield; it $b_{12.5}$ 82–6° in H (slight resinification), seps. from petr. ether in needles with a pleasant odor distinctly different from that of A, m. about 75–80°, gives no color with $FeCl_3$, changes in the air in a few hrs. to a viscous yellowish oil, is stable longer in a H atm.; *phenylurethan*, long needles from dil. alc., m. 121.6–2.0°. Boiled 15 min. under a reflux with 10% HCl the cyclol yields A, as also, by intramol. rearrangement, when it is slowly heated in dry H until its temp. remains const. at 193°, the m. p. of A. Attempts to bring about the reverse change, the enolization of A, by heating with Ac_2O (even after 8 hrs. at 160° in the presence of NaOAc) left the A unchanged, owing to the fact that the acetate of the cyclol is formed too slowly; this acetate was obtained in traces only, as an oil with an odor like that of isobornyl acetate, from the cyclol and Ac_2O. PCl_5 replaces the HO group of the cyclol with Cl but the HCl formed at once adds to the product, with rupture of the trimethylene ring, and the only product which could be isolated was a small amt. of camphenilone

dichloride, m. 168–9°. CH_2N_2 in Et_2O does not attack the cyclol even after 2 days. When 1.8 g. of the alc. in 20 cc. Et_2O is treated with 0.9 g. Na wire, boiled gently for 12 hrs., removed from the excess of Na and boiled under a reflux for 12 hrs. with an excess of MeI there are obtained a small fraction, b_{10} 60–70, of an oil with a not unpleasant odor, possibly the desired *apotricyclyl methyl ether*, and, chiefly, a fraction b_3 about 160°, slowly depositing crystals, m. 146–66°, of camphenilonepinacol, while the oily portion, on renewed fractionation, gives the *dimethyl ether* of the pinacol; with Me_2SO_4, only the ether and none of the free pinacol is obtained. The action of the Na on the cyclol, therefore, results in the formation of the compd. II.



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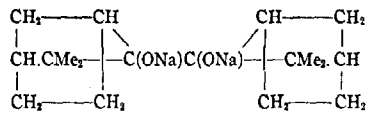


II

CHAS. A. ROUILLER

Sesquiterpene compounds. I. Preparation of a naphthalene derivative from cadinene. L. RUZICKA AND JULES MEYER. *Helvetica Chim. Acta* **4**, 505–10(1921).—The only compd. in the sesquiterpene series of known constitution is the aliphatic alc. (sesquiterpene) farnesol, due to Kerschbaum (*C. A.* **7**, 2753). In the α-santalene series no constitutional formulas have been detd. although much work has been carried out on these compds. In detg. constitution $KMnO_4$ and O_3 have been much used for the production of identifying compds. but R. and M. proposed using dehydrogenation methods for this work. Capitaine and Soubeiran (*Ann.* **34**, 324(1840)) reported a compd. having the appearance and odor of $C_{10}H_8$ by heating cadinene dihydrochloride, and Semmler (*Ber.* **36**, 103(1903)) mentioned obtaining a $C_{10}H_8$ deriv. from sesquiterpenes. R. and M. heated cadinene (A) with S, a reagent which with abietic acid gave retene, according to Vesterberg (*Ber.* **36**, 4200(1903)). A ($C_{15}H_{24}$) + 3S = $C_{15}H_{18}$ + $3H_2S$. **A**, b_{12} 125–38° (from Schimmel), in ether satd. with HCl at 0° gave the dihydrochloride, colorless needles from EtOAc, m. 116–8°, and when this product was treated with alc. NaOH pure **A**, b_{13} 134–6°, was obtained. 70 g. A with 33 g. powdered S were heated 6 hrs. at 200° and finally at 250° and after all the H_2S had been evolved by distn. *in vacuo* 50 g. yellow oil b_{12} 148–58°, were secured. This oil was purified through the picrate and by this treatment its compn. was not altered. A hot satd. alc. soln. of picric acid gave the picrate, crystals, m. 115°, which when heated with strong NH_4OH and distd. over Na gave an oil b_{12} 157–8°, b_{730} 291–2°, *the hydrocarbon* $C_{15}H_{18}$. The *picrate*, orange-yellow needles, from alc., m. 115°, and the *styphnate* yellow needles from alc., m. 138°, was prepd. by treating C with 1 mole trinitroresorcinol in alc. When 10 g. C in 10 g. alc. were warmed with 7 g. Na with gradual addition of 100 cc. abs. alc. the mixt. was poured into acidulated water, ether-extd. and a colorless *oil*, $C_{15}H_{20}$, b_{12} 151–3°, was obtained. Dil. $KMnO_4$ was decolorized in the cold after shaking for a short time and the picrate could not be formed. H. E. WILLIAMS

The influence of carbon disulfide in the Friedel-Crafts synthesis. P. J. MONTAGNE. Univ. Leyden. *Rec. trav. chim.* **40**, 247–8(1921).—CS_2 is used in the Friedel-Crafts synthesis as a solvent and diluent and serves to regulate the reaction temp. at a low level. When CS_2 is used in the synthesis of 4-$MeOC_6H_4COPh$ by the Friedel-Crafts reaction from 4-$MeOC_6H_4COCl$ and C_6H_6 the reaction is spoiled. A good result is obtained when CS_2 is omitted. M. thinks that the poor result of Petersen (*C. A.*

5, 3800) in this synthesis is due to the fact that he added CS_2 while Ullman and Goldberg (*Ber.* **35**, 2814(1902)) who omitted CS_2 obtained good results. Olivier (*C. A.* **8**, 3013) previously recognized the influence of CS_2 in this synthesis and discussed it. E. J. W.

Hydrobenzoin, semihydrobenzoin, and semipinacolin transpositions. Study of the dehydration of alkylhydrobenzoins. M. Tiffeneau and A. Orékhoff. *Bull. soc. chim.* **29**, 422-9(1921); cf. *C. A.* **1**, 728; *Ann. chim. phys.* **10**, 345(1907).—The dehydration $PhRC(OH)CH(OH)Ph \longrightarrow Ph_2RCCHO$ was applied to 2 hydrobenzoins. 25 g. PhMeC(OH)CH(OH)Ph added to 200 cc. concd. H_2SO_4 at 0°, let stand 2 hrs. at room temp., poured into 2 l. H_2O, extd. with Et_2O, dried with Na_2SO_4 and evapd., yields 18 g. $Ph_2MeCCHO$, m. 58–9°. Oxime prepd. by the ordinary methods, m. 124–5°. *Semicarbazone*, small needles from hot EtOH, m. 214–5°. Dehydration of PhEtC(OH)CH(OH)Ph (**A**) by cold concd. H_2SO_4 has been described previously (*C. A.* **15**, 2195). 40 g. of **A** boiled with 600 cc. dil. H_2SO_4 for 3 hrs., extd. with Et_2O, washed with NaOH and H_2O, dried with Na_2SO_4 and evapd., yields 33 g. of $Ph_2EtCCHO$ (**B**), an oily mass, b_{20} 192–4°. Semicarbazone (**C**), fine needles from EtOH m. 175–6°. Oxime, small white crystals from EtOH, m. 131–2°. B regenerated from C is a very thick yellowish oil, refusing to cryst. at a low temp. 7 g. $AgNO_3$ in 7 cc. H_2O added to 5 g. of **B** in 100 cc. EtOH, slowly treated with 5 g. KOH in 50 cc. H_2O, let stand 1 day, filtered, washed with cold H_2O, satd. with CO_2, concd., acidified with H_2SO_4, filtered and dried, yields on analysis an oxidation product, $C_{16}H_{16}O_2$, m. 172–3°.

C. C. Davis

The hydrobenzoin and semipinacol transpositions of propylhydrobenzoin and butylhydrobenzoin. Frédéric Billard. *Bull. soc. chim.* **29**, 429-45(1921); cf. *C. A.* **3**, 1277; **12**, 2539; **13**, 1580–1, 2195; **14**, 2623; **15**, 1497.—This paper reports a continued study on the mol. rearrangements on dehydration of alkylhydrobenzoins and deals with *PhPrC(OH)CH(OH)Ph* (**A**) and *PhBuC(Oh)CH(OH)Ph* (**B**). **A** was prepd. in 64% yield from benzoin and PrMgI in dry ether by heating 3–4 hrs. on the water bath. Water was added and the **A**, recovered from the ether by distn., crysts. from alc., m. 119°. When treated at 0° for 1 hr. with concd. H_2SO_4, **A** gave a mixt. of *1, 1-diphenyl-2-pentanone*, $Ph_2CHCOPr$ (**C**), b_{13} 185–92°, *semicarbazone* m. 191–2°, 107° *oxime* m and propyldesoxybenzoin, PhPrCHCOPh (**D**), m. 33–4°, *semicarbazone* m. 124–5°. The ratio of semicarbazones of **C** and **D**, by which the sepn. of the two compds. was effected, was 11.5 to 1. Identification was completed by the method of detg. the m. p. of mixts. of the compd. with a synthesized sample. When boiled for 6–7 hrs. with melted hydrated $(CO_2H)_2$ **A** gave an oil b_{16} 185–200°, which was a mixt. of **C** and *1,1-diphenylpropylacetaldehyde*, $Ph_2PrCCHO$ (**E**), b_{16} 189–91°, *oxime* m. 117°, *semicarbazone* m. 139°. By 6 hrs. boiling with dil. H_2SO_4 (1:4), **A** was converted into **E**. **B**, m. 125°, was prepd. from BuMgI and benzoin as given above and crystd. from alc. Yield 68%. Treated with concd. H_2SO_4 (4 parts) at 0° for 1 hr, **B** yielded *butyldesoxybenzoin* (**F**), PhBuCHCOPh, m. 64°, which gave no oxime or semicarbazone but was converted into *1,1,2-tripheryl-1-hexanol*, m. 114–5°, and *1,1-diphenyl-2-hexanone*, $BuCOCHPh_2$, m. 38°, *oxime* m. 80°, *semicarbazone* m. 159°. With dil. H_2SO_4 (1:4), **B** is altered very slowly. Dild. to 3 vols. H_2SO_4 appeared to change the reaction products. No results of the expts. are given. With $(CO_2H)_2$ **B** yielded a little **F** and much *diphenylbutylacetaldehyde*, b_{13} 194–6°, *oxime* m. 110°, *semicarbazone* m. 153°. The two *n*-alkylhydrobenzoins studied resemble, therefore, the Et deriv. when treated with the dehydrating agents stated and are unlike the Me and iso-Bu derivatives in that respect.

R. L. Brown

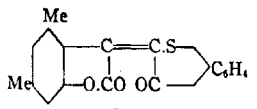
1,8-Dihydroxynaphthalene. Gustav Heller and Hugo Kretzschmann. Univ. Leipzig. *Ber.* **54B**, 1098–1107(1921).—1,8-$C_{10}H_5(OH)_2$ (**A**) is obtained in colorless form, m. 140°, from 50 g. com. 1,8,4-$C_{10}H_4(OH)_2SO_3H$ in 500 cc. H_2O heated 1 hr.

at 150° with 25 cc. of concd. H_2SO_4, cooled, filtered, taken up in sufficient hot H_2O and treated with CO_2; 1.6 g. in 60 cc. of 80% alc. and 5 g. of 10% HCl treated in ice with 1 mol. PhN_2Cl yields quant. *4-benzeneazo-1,8-dihydroxynaphthalene* (B), dark aggregates with greenish shimmer from alc., m. about 185° but after further recrystn. only slightly sinters about 220–30°, does not m. 260°, seps. from AcOH at once in fine needles without any distinct m. p., moderately sol. in the various solvents with deep red, completely in dil. alkali with cherry-red color. If the coupling is carried out in AcOH (A in 100 parts H_2O and a little soda added to PhN_2Cl, NaOAc and AcOH), the dye soon begins to sep. in red-violet form, about 90% of which is identical with B but the other 10 % is insol. in alkali; similarly in soda soln. the product consists mainly of B but about 7.5 % is insol. in alkali and alc. and in it by conversion into the Bz deriv. can be identified the disazo compd. *4,5-Disazobenzene-1,8-dihydroxynaphthalene* (C), from a diazo soln. from 5.88 g. $PhNH_2$ containing 2.7 g. AcOH and 22 g. NaOAc slowly treated with 4.8 A, 480 cc. H_2O and 2.3 g. Na_2CO_3 and stirred 3 hrs. (yield, 8.5 g.), m. about 238°, sol. in concd. H_2SO_4 with violet-blue color. Coupling with 2 mols. diazotized $PhNH_2$ in soda soln. also leads to a mixt. of B and of alkali-insol. products (5.8 g.) from which no homogeneous product could be isolated by extn. with alc.; the alc.-insol. portion (3.8 g.) m. about 208°, contains 12.76% N and on reduction with alk. $Na_2S_2O_4$ and benzoylation yields yellowish brown cryst. granules, darken about 250°, sinter 260°, m. 268°; this differs from any of the Bz derivs. described below so that in the coupling some isomeric disazo dye has apparently been formed. *4-Benzenesulfonylazo-1,8-dihydroxynaphthalene* (D), from A and diazotized sulfanilic acid in acid soln., fine brown-black needles from H_2O-HCl, sol. in alkalies with wine-red, in concd. H_2SO_4 with steel-blue color, dyes wool a deep cherry-red, Al-mordanted wool in more bluish tones and Cr-mordanted wool a deep dark brown; coupled with diazotized $PhNH_2$ in soda soln. it changes to a dark brown-red and concd. HCl ppts. a black dye sol. in hot H_2O with a bronze color and yielding on reduction and benzoylation products m. 236° and 268°; if the coupling is carried out in AcOH the product is likewise not homogeneous. *Tribenzoyl-4-amino-1,8-dihydroxynaphthalene*, from 2.64 g. B, 25% NaOH (4 mols.) and 3 mols. $Na_2S_2O_4$ digested at 60–70°, filtered, treated with more NaOH and shaken in the cold with BzCl, gray-white leaflets from AcOH, m. 236°, also obtained from D. *Tetrabenzoyl-4,5-diamino-1,8-dihydroxynaphthalene*, from 1.2 g. of C, 7 g. $Na_2S_2O_4$ and 2.5 g. NaOH on the H_2O bath and subsequent treatment with 8 g. BzCl, needles from AcOH, decomps. 246°. *8-Hydroxy-1,2-naphthoquinone 2-oxime*, from A in 60 parts H_2O and a little soda with 1 mol. $NaNO_2$ acidified at 0° with AcOH, brownish yellow needles from C_6H_6, darkens 170°, decomps. 183°, deflagrates on rapid heating; the soda soln. is yellow and seems to contain an equil. mixt., for it is colored a stronger reddish yellow by free alkali. The oxime dissolves in concd. HCl with orange-red, in H_2SO_4 with cherry-red color and gives in alc. with $FeCl_3$ a dark brown-violet color; 0.9 g. in dil. NaOH with 2.8 g. BzCl gives a brown ppt., the filtrate from which with more BzCl yields a yellow-brown product sepg. from C_6H_6 in elongated yellow leaflets, m. 177°, easily sol. with yellow color in AcOH, C_6H_6 and alc., in concd. H_2SO_4 with cherry-red color; it consists of *dibenzoyl-8-hydroxy-1,2-naphthoquinone 2-oxime*. The first ppt., *dibenzoyl-1,8-dihydroxy-2-nitrosonaphthalene*, is formed in smaller amt.; it seps. from AcOH in gray-white leaflets, m. 203°, sol. in H_2SO_4 with cherry-red color, only slowly decompd. by hot NaOH. *Tribenzoyl-2-amino-1,8-dihydroxynaphthalene*, from 2 g. of the oxime in 20% NaOH reduced with $Na_2S_2O_4$ at 50–60°, filtered protected from the air and treated with 7 g. BzCl (yield, 4 g.), cryst. powder from alc., m. 201°. *1,8-Dihydroxy-2-naphthaldehyde*, from 5 g. A, 6 g. $ZnCl_2$ and 12 cc. anhydrous HCN in 50 cc. Et_2O satd. with HCl in ice, allowed to stand 2 days, filtered and decompd. with H_2O (yield, about 20%), yellow needles, turns green 110°, black 170°, sol. in H_2SO_4 with

yellow-brown color changing to green on long standing, gives in alc. with $FeCl_3$ an olive-green flocculent ppt.; *phenylhydrazone*, crystals from AcOH-H_2O, does not m. 285°, sol. in soda with violet, in H_2SO_4 with yellow-brown color. *Dibromo-1,8-dihydroxynaphthalene* (0.8 g. from 0.8 g. **A** in 6 cc. AcOH slowly treated with Br), seps. from $CHCl_3$, when crystd. quickly, in needles, begins to darken 130°, evolves light brown vapors about 150°, dissolves easily in soda but a brown color soon appears, dissolves with great difficulty in H_2O and also in concd. H_2SO_4 but on heating forms a red-violet soln., gives in AcOH with $FeCl_3$ olive-green flocks. *1,8-Dimethoxynaphthalene* (0.5 g. from 1 g. **A** in 20 cc. H_2O and 3 g. calcined soda shaken with 3 g. Me_2SO_4 and heated to 40°), leaflets from petr. ether, m. 50°, volatilizes without decompn. at a high temp., sol. in H_2SO_4 with golden yellow color. C. A. R.

A new method of preparation of coumarandiones. R. Stollé and E. Knebel. *Ber.* **54B**, 1213–20(1921); cf. *C. A.* **8**, 2167.—The extension of the study of the action of $AlCl_3$ in CS_2 to other aryl oxalyl chlorides besides $ClCOCO_2Ph$ has shown that the yields of the corresponding substituted *o*-benzoylformic acids or coumarandiones are the better the more stable the latter, this stability agreeing with the generalizations established by v. Auwers for the stability of the coumaranone ring, which "is increased by substituents in the *m*-position to the O and weakened by *o*- and *p*-substituents." PhOCOCOCl, from 19 g. PhOH and 32 g. $(COCl)_2$ in Et_2O, b_{12} 97°, m. 57°, characterized by conversion with $PhNH_2$ in Et_2O into *phenyl oxalanilide*, needles from alc., m. 137°, also obtained from PhNHCOCOCl and PhOH in hot C_6H_6. *Phenyl oxal-p-toluidide*, from PhOCOCOCl and *p*-$MeC_6H_4NH_2$, needles from alc., m. 155°. From 10 g. PhOCOCOCl in 50 cc. CS_2 dropped into 20 g. $AlCl_3$ in 150 cc. CS_2 and allowed to stand 36 hrs. are obtained 4 g. *o*-$HOC_6H_4CO_2H$ and 2.6 g. *o*-$HOC_6H_4COCO_2H$ (as the phenylhydrazone). *p-Cresyl oxalyl chloride*, from *p*-cresol and $(COCl)_2$, yellow oil solidifying on cooling, b_{13} 115°, gives with $PhNH_2$ *p-cresyl oxalanilide*, needles from alc., m. 132°, and with $AlCl_3$ 5 g. yields 3 g. *p*-cresotic acid and 0.5 g. 5,2-$Me(HO)C_6H_3COCO_2H$ (as the phenylhydrazone). *m-Cresyl oxalyl chloride*, light yellow oil, b_{14} 120°; *anilide*, crystals from alc., m. 94°. With $AlCl_3$ 10 g. of the chloride gives 6 g. 6-methylcoumarandione and 0.75 g. *m*-cresotic acid, m. 175°, which is also formed when the dione is treated with H_2O_2 in alk. soln. *sym-m-Xylenyl oxalyl chloride*, yellow oil, b_{12} 128°; di-*m*-xylenyl oxalate, from $(COCl)_2$ and 2 mols. of the xylenol, m. 157° (Bischoff and Hedenström, *Ber.* **35**, 3444(1902), give 144°); *sym-m-xylenyl oxalanilide*, leaflets from alc., m. 113°. The chloride with $AlCl_3$ gives 90% of *4,6-dimethylcoumarandione*, bright yellow needles from ligroin, m. 144°, sublimes in long yellow spears; the orange-yellow NaOH or soda soln. is transiently decolorized by acids but the dione quickly seps. again and is also pptd. by H_2O from the brown-red soln. in concd. H_2SO_4. Alk. H_2O_2 oxidizes the 4,6,2-$Me_2(HO)C_6H_2COCO_2H$ to 4,6,2-$Me_2(HO)C_6H_2CO_2H$, m. 166°. The dione in AcOH and a few drops concd. HCl on the H_2O bath easily condenses with β-hydroxythionaphthene to the *compound* **I**, bright red silky needles from AcOH, m. 225°, and with indoxyl to the *compound* **II**, dark violet-brown needles from AcOH, m. 255°. Equal amts. of the dione and 4,6-dimethylcoumaranone heated 4 hrs. under a reflux in AcOH with a little concd HCl give pale yellow needles from AcOH, having the compn. of *4,6,4',6'-tetramethyloxindirubin* (**III**), although such a compd., according to the observations of Fries and Fink (*C. A.* **3**, 649), should have a characteristic color; it m. 233° and dissolves on gentle warming in alc. KOH with red-yellow color, dil. HCl producing an orange-red ppt. which seps. from AcOH in red rhombic leaflets m. 218°. *p-Chloro-sym-m-xylenyl oxalyl chloride*, m. 51°, b_{13} 157°; *anilide*, spears from alc., m. 160°; *bis-p-chloro-sym-m-xylenyl oxalate*, felted needles from alc., m. 156°. The chloride with $AlCl_3$ gives a good yield of *5-chloro-4,6-dimethylcoumarandione*, bright yellow needles from ligroin, m. 121°, sublimes without decompn., gives with alk. H_2O_2

5-chloro-4,6-dimethyl-2-hydroxybenzene-1-carboxylic acid, long needles from H_2O, m. 193°, gives a blue-violet color with $FeCl_3$ in H_2O. The dione easily condenses in hot AcOH and a few drops concd. HCl with indoxyl to the **dye IV**, dark violet-brown needles from AcOH, m. about 305° (decompn.). *p-Xylenyl oxalyl chloride*, light yellow oil, b_{14} 124°; *anilide*, leaflets from alc., m. 120°. The chloride with $AlCl_3$ gives a good yield of *4,7-dimethylcoumarandione*, yellow prisms from Et_2O, m. 136°, sol. in concd. H_2SO_4 with yellow-red color, repptd. unchanged from the orange-yellow alkali or alkali carbonate solns., oxidized by alk. H_2O_2 to *3,6-dimethyl-2-hydroxybenzene-1-carboxylic acid*, long silky needles from H_2O, easily volatile with steam, gives a blue-violet color with aq. $FeCl_3$.



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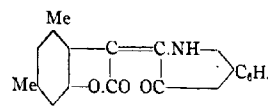

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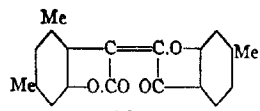

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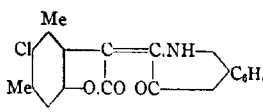


IV

CHAS. A. ROUILLER

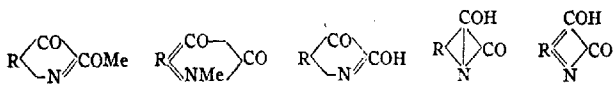
Comparative preparation of derivatives of isatin, phthalimide, succinimide and *o*-hydrazinobenzoic anhydride. GUSTAV HELLER AND PAUL JACOBSOHN. Univ. Leipzig. *Ber.* **54B**, 1107–17(1921); cf. *C. A.* **12**, 2563.—It had been found that Et isatin-*N*-carboxylate heated with alc. takes up 4 atoms of H and rearranges into 2,3-dihydroxy-2-carbethoxydihydroindole. To det. how general the reaction is the *N*-carbethoxy derivs. of a number of substituted isatins have been similarly treated. *Ethyl 5-bromoisatin-N-carboxylate*, from equimol. amts. of Na 5-bromoisatin, in 3 parts C_6H_6, and $ClCO_2Et$ heated 1 hr. at 40–5°, light yellow prisms from C_6H_6 and ligroin, m. 161°, gives a deep blue indophenin reaction; 1 g. boiled under a reflux 5–6 hrs. with 5 parts abs. alc. yields 0.7 g. *α,β-dihydroxy-α-carbethoxy-5-bromodihydroindole*, light yellow leaflets, gives no indophenin reaction, also formed when the *N*-carboxylate is allowed to stand 10 days in C_6H_6 (conditions under which the unsubstituted Me and Et esters remain unchanged) or when it is heated 2 days on the H_2O bath with 6 parts H_2O. *Ethyl 5-chloroisatin-N-carboxylate* (1.3 g. from 9 g. Na chloroisatin), crystals from C_6H_6 and ligroin, m. about 82°, gives the indophenin reaction, converted by boiling 1 hr. with 5 parts alc. into *α,β-dihydroxy-α-carbethoxy-5-chlorodihydroindole*, light yellow 4-cornered tablets (80% yield), m. 87°, could not be obtained by letting the *N*-carboxylate stand with 50% H_2SO_4 or by heating it to 50–60°. The analogously constituted derivs. of $C_6H_4(CO)_2NH$ were then tried. *N-Carbethoxyphthalimide* (3.2 g. from 5.55 g. powdered $C_6H_4(CO)_2NK$ in 5 parts C_6H_6 boiled 1.5 hrs. with 4.5 g. $ClCO_2Et$ and allowed to stand 18 hrs.), crystals from C_6H_6-petr. ether, m. 87–9°, sol. in concd. HCl and repptd. unchanged on immediate addition of H_2O but converted into $C_6H_4(CO_2H)_2$ on standing 24 hrs. or heating, unchanged by boiling several hrs. with 5 parts alc. or by 50% H_2SO_4 in the cold or at 40–50°; 2 g. treated with 11 cc. of 8% NaOH, then neutralized with 8% HCl and cautiously treated with more HCl, yields *N-carbethoxyphthalamic acid* (also obtained by heating the *N*-carboxylate with 6 parts H_2O on the H_2O bath until it dissolves), needles from H_2O or C_6H_6, begins to sinter about 55°, partly m. 66°, m. completely about 70° if plunged into a bath at 60°. Ag phthalimide, obtained at once as a cryst. ppt. with 0.5 H_2O from the K salt and $AgNO_3$ in H_2O, dis-

solves very easily in NH_4OH, does not m. 300°. A Ag salt of the same compn., which is powdery and dissolves in NH_4OH only on warming, is obtained by adding 12 g. AgOAc in 400 g. hot H_2O to 12 g. $C_6H_4(CO)_2NH$ in 250 cc. hot alc. From 7.6 g. of the salt prepd. from $AgNO_3$ heated 1.5 hrs. in 35 g. C_6H_6 with 4.5 g. $ClCO_2Et$, filtered warm and dild. with 2 vols. petr. ether is obtained 2.1 g. *O-carbethoxyphthalimide*, fine needles from petr. ether, m. 126–7°, insol. in cold HCl and converted into $C_6H_4(CO_2H)_2$ on heating or by dissolving in dil. NaOH or boiling with H_2O, gives $C_6H_4(CO)_2NH$ when boiled 3 hrs. with alc. Under the same conditions the salt prepd. from AgOAc gave only $C_6H_4(CO)_2NH$. *N-Carbethoxysuccinimide* (2.2 g. from 2.8 g. $(CH_2CO)_2NK$ and 2.3 g. $ClCO_2Et$ refluxed 1 hr. in 16.8 g. C_6H_6), crystals from Et_2O and ligroin, m. 44°, unchanged by boiling several hrs. with alc., forms $(CH_2CO_2H)_2$ on standing in HCl; allowed to stand 1 hr. in moderately dil. NaOH and cautiously treated with HCl or heated 2 hrs. on the H_2O bath with 6 parts H_2O it yields *N-carbethoxysuccinamidic acid*, crystals from Me_2CO and petr. ether, m. 161°, hydrolyzed on standing in concd. NaOH and HCl, unchanged by boiling with alc. *O-Carbethoxysuccinimide* (0.6 g. from 4.2 g. of the Ag salt of the imide (prepd. from the K salt and $AgNO_3$) heated on the H_2O bath in 16 g. C_6H_6 with 2.3 g. $ClCO_2Et$), tables from C_6H_6 and petr. ether, m. 110–2°, easily changes in the air, gives $(CH_2CO)_2NH$ on boiling 1.5 hrs. with alc., heating 1 hr. on the H_2O bath with 6 parts H_2O or standing a short time with dil. NaOH. When 27.4 g. o-$H_2NC_6H_4CO_2H$ in 136 g. H_2O and 2.25 mols. concd. HCl are diazotized and poured into 105 g. Na_2SO_3 in 420 g. H_2O containing 24 g. NaOH, treated the next day with 35 cc. AcOH, reduced with Zn dust at room temp., filtered, treated with 20 cc. concd. HCl, filtered after 24 hrs., treated with 100–50 cc. fuming HCl and allowed to stand some days, there is obtained 30 g. o-$HO_2CC_6H_4NHNH_2.HCl$; if the salt is treated with NaOAc at room temp. it deposits the free acid in almost pure form but if the hot concd. soln. is treated with the calcd. amt. of NaOAc and concd. somewhat the anhydride (**A**) is deposited and seps. from alc. in almost colorless crystals, darken 220°, m. 242° (decompn.), slowly sol. in dil. soda, does not reduce Fehling soln. even on heating and gives in alc. with $FeCl_3$ a blue-violet color soon changing to dirty green. *N^2-Benzoyl-o-hydrazinobenzoic acid*, obtained with BzCl in C_5H_5N, prismatic needles from alc., m. 255–6°, gives in alc. with $FeCl_3$ a transient dark red color, splits off BzOH when heated with concd. H_2SO_4 on the H_2O bath; heated 2 hrs. on the H_2O bath with 4 parts Ac_2O it yields *N^1-acetyl-N^2-benzoyl-o-hydrazinobenzoic anhydride*, rhombic plates from alc., m. 126–7°; if the expt. is repeated and the mixt. is refluxed, the product is Fischer's N^1,N^2-Ac_2 compd., which is deacetylated by heating 2 hrs. with alc. NaOH. *N^1,N^2-Dibenzoyl derivative* (1.6 g. from 1.3 g. of **A** and 6.5 g. BzCl in 16 g. C_5H_5N), prismatic needles from alc., m. 106°, hydrolyzed back to **A** by alc. NaOH; 1 part heated 2 hrs. over a free flame with an equal amt. of fused NaOAc and 5 parts Ac_2O gives the di-Ac deriv. *1-Carbethoxy-o-hydrazinobenzoic anhydride* (*1-carbethoxy-3-keto-1,3-dihydroindazole*) (0.8 g. from 1.6 g. $ClCO_2Et$ dropped into 1.3 g. of **A** in 12 g. cold C_5H_5N), fine needles from AcOEt, m. 193°, is turned yellow to brown by dil. NaOH on the H_2O bath but acids reppt. some of it unchanged, likewise after heating 1.5 hrs. with HCl; it is not affected by HNO_2, gives in alc. with $FeCl_3$ a permanent red color, titrates as a monobasic acid, is unchanged by boiling alc. *1-Carbomethoxy homolog*, needles from AcOEt, m. 198°, shows no tendency to add H and gives a red $FeCl_3$ reaction, forms in alc. with $AgNO_3$ a gelatinous ppt., converted by heating 1 hr. with NaOAc and Ac_2O into (o-$AcNHNAcC_6H_4CO)_2O$. CHAS. A. ROUILLER

Isocurcumin. III. GUSTAV HELLER. Univ. Leipzig. *Ber.* **54B**, 1118–9(1921); cf. *C. A.* **12**, 702.—In a continuation with other aldehydes of the investigation of the reaction whereby β-isocurcumin is formed in small amt., together with larger amts. of the non-homogeneous α-isocurcumin, from vanillin and CH_2Ac_2, it has been found

that the alc. HCl used decomps. the CH_2Ac_2 to a considerable extent into Me_2CO, which combines with the aldehyde and HCl to salt-like analogs of $CO(CH:CHPh)_2$, and in a number of cases it was these salts which were isolated while the CH_2Ac_2 condensation products were uncrystallizable and remained in the mother liquors. As the problem has in the meantime been solved by the synthesis of curcumin (Lampe, *C. A.* **13**, 715) this investigation will not be continued. From 9.8 g. *p*-HOC_6H_4CHO in 8 g. alc. and 4 g. CH_2Ac_2 treated in ice with 8 g. satd. alc. HCl is obtained 1.5 g. of an HCl salt giving in alc. on addition of H_2O or NaOAc (*p*-$HOC_6H_4CH:CH)_2CO$. Similarly with thymolaldehyde is obtained the *hydrochloride*, green needles, of *dithymolaldehydeacetone*, reddish yellow crystals with violet surface luster from AcOH or alc., m. 268°, sol. in concd. H_2SO_4 with crimson and in NaOH with bluish red color and forms with concd. NaOH a dark red salt, reconverted into the aldehyde by boiling KOH; *diacetate*, m. 129°. CHAS. A. ROUILLER

The true and alleged isomerisms in the isatin series. A. HANTZSCH. *Ber.* **54B**, 1221–57(1921); cf. Heller, *C. A.* **15**, 87, and earlier papers.—Of Heller's alleged three isomers of isatin, only one, isatol, really exists. On methylation of isatin there is formed from the Ag salt primarily only a single, well crystd. ether, v. Baeyer's isatinol Me ether (I); from this there is formed secondarily, *e. g.*, on warming in C_6H_6, by isomerization the *N*-Me ether (II); the sapon., which occurs with exceeding ease, being produced even by H_2O at room temp., never yields the corresponding isatinol (III) but, by spontaneous isomerization, isatin or isatol. Isatin is formed chiefly in aq. alc. soln., isatol from the solid ether by the moisture of the air, yielding quant. at first the metastable α-isatol (probably IV), which exists only in the solid form and is converted by all solvents into the stable β-isatol (probably V); this is also formed chiefly (together with some isatin) on sapon. of the isatinol ether in acid aq. alc. soln., but concd. acid splits off the MeO group with formation of isatin. That the free isatols are separate isomers and not, like the isatinols, merely tautomers is explained by the fact that they no longer contain the grouping $-N:C(OH)-$, which can change over into $-NH.CO-$. Heller's "isatol," which he describes as an isomer of isatin, is no chem. individual but an impure β-isatol. His "isatinone," which he later comes to consider as a "methylisatoid" and not an isomer of isatin, is in fact the only isomer of isatin which exists and is identical with β-isatol. Also v. Baeyer's other alkylisatoids and Heller's numerous other alleged new isomers of isatin and 5,7-dimethylisatin do not exist, especially the supposed lactim or enol form, dimethylisatol; in this series also dimethylisatol is the only isomer of dimethylisatin. Consequently the isomerisms in the isatin series are in full accord with Hantzsch's observations and theories on isomerism, tautomerism and salt formation. To obtain good yields in the action of MeI on Ag isatin it is important to start with the



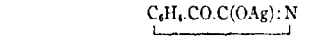
I II III IV V

purest possible materials, as slight impurities partially lead with ease to the secondary products owing to decompn. of the I first formed and partially make more difficult the isolation and purification of the I. The prepn. of the Ag salt is described in the following abstr. The MeI is best prepd. fresh every time from KI and Me_2SO_4 and fractionated from $CaCl_2$; in all the following expts. it was used in slight excess. To prep. I, Ag isatin and MeI are allowed to stand in a little C_6H_6 in the dark in a closed vessel, protected from moisture, with frequent shaking until all of the Bordeaux-red salt has been converted into yellow AgI (8–14 days), dild. with more dry C_6H_6, filtered, evapd. in a dark vacuum desiccator over paraffin, pressed on clay, again dissolved in a

little C_6H_6 and allowed to cryst. very slowly (14 days) in the dark over paraffin. Only in this way can the formation of the yellow so-called "methylisatoid" be almost wholly prevented and the pure I be obtained in red prisms, m. 101–2°. While it can, in the form of compact crystals, be kept for years in the air without apparent change, in powder form it decomps. in air and light in the course of a few days into the light yellow IV, m. 238–40°, according to the equation $I + H_2O \longrightarrow IV + MeOH$. On the other hand, on warming with 50% aq. alc. there is obtained, instead of the expected III, its isomerization product, isatin, which is also obtained by evapg. a C_6H_6 soln. of I on the H_2O bath; sometimes, by cautiously evapg. the soln. several times on a sand bath, *i. e.*, in a dry atm., the I can be quant. converted into II. Large, well developed and uninjured crystals can be kept a long time in the brightest sunlight in moist air without change, which can only be explained by assuming that such crystals are protected by an imperceptible thin layer of IV. IV (Baeyer's "methylisatoid") is prepd. by stirring 3 g. of well dried and powdered Ag isatin with an equal wt. of pure MeI, boiling gently 20–30 min. under a reflux, adding 30 cc. dry C_6H_6 and a little charcoal, bringing to a boil, filtering into an open dish and allowing to evap. spontaneously in the air and light (best sunlight); it seps. as a light yellow powder and as on recrystn. it changes into V it can be purified only by breaking it up with a spatula and carefully stirring it with a little Et_2O, decanting, repeating the process, quickly warming a little with C_6H_6, filtering, and repeating the process until a sample m. 238–40° (decompn.); yield, 30%, calcd. on the basis of the amt. of Ag salt used. It is indefinitely stable in the solid form but is recovered from all solns., even when heating is avoided, only in the form of the darker V. It dissolves in NaOH with formation of a red salt of V; in the solid form it is indifferent towards N_2CHCO_2Et but in Et_2O distinctly evolves N and must, therefore, contain a phenol-like HO group; shaken with C_6H_6 containing thiophene and concd. H_2SO_4 it does not give the blue indophenin reaction, even on gentle warming, but only a dark red-brown color That it really has the compn. IV and not that, $C_{17}H_{12}O_4N_2$, of Baeyer's methylisatoid is shown by the fact that 0.1153 g. simply dissolved in alc. and evapd. to dryness gives 0.1155 g. pure V, m. 226°. Further evidence of the absence of any MeO is afforded by the fact that when covered with concd. HCl and evapd. to dryness over KOH it takes up 0.5 mol., forming the red isatol hydrochloride, $C_8H_5O_2N.0.5HCl$, which, however, loses its HCl again, very slowly at room temp., in 1 hr. at 85–7°, the IV at the same time rearranging into V. V (Heller's isatinone) can be prepd. without purifying the intermediate IV; the C_6H_6 soln. of the product of the reaction of Ag isatin on MeI is evapd. to dryness, washed with Et_2O, extd. with warm C_6H_6, dissolved in alc., boiled with charcoal and concd. It can also be obtained with EtI instead of MeI; in this case the intermediate IV could never be isolated. With concd. HCl it forms the same red salt as IV. While its red alkali salts are readily sol. and hydrolyzed to a large extent in H_2O the Ag salt is easily obtained by treating V in alc. with a slight excess of alc. $AgNO_3$ and then slowly with somewhat more than the calcd. amt. of NaOH; the salt is red and dissolves with yellow color in pyridine and piperidine. Heller's "isatinol" could never be obtained from the alk. soln. of V with 50% AcOH, pure V being at once recovered under the most varied conditions. V is indifferent towards N_2CHCO_2Et but is smoothly converted by CH_2N_2, with evolution of N, into the Me ether. All attempts to obtain Heller's "isatil," m. 194.5°, using Ag isatin prepd. in various ways but only the purest BzCl, failed; the prepns. obtained m. around 180° and proved not to be homogeneous. H. was able to show, however, with a small sample of Heller's own product which he had that it was only impure V; it depressed the m. p. of V only 1.5°, that of isatin 14°, and added HCl (approx. 0.5 mol.) with formation of a dark red salt. Similarly Ag 5-chloroisatin with BzCl gave in only one case a small amt. of deep red crystals m. 186° but on recrystn. from pure

Me_2CO at room temp. these yielded ordinary 5-chloroisatin, m. 243°, and much BzOH. 5-Bromoisatol, from Ag bromoisatin and MeI or EtI, prismatic crystals from alc., m. 247°; the fact that the products obtained in the two ways are identical shows that they cannot be "methyl-" and "ethylbromoisatoids;" this is also confirmed by the Br content (35.43%) of the product obtained with MeI; it does not add HCl under the same conditions as V. In the 5,7-dimethylisatin series Heller's supposed isomers were investigated only on samples supplied by him. As some of them were certainly isatol derivs. they were subjected to the reaction whereby isatol can be distinguished most sharply from isatin and freed most rapidly from impurities and which depends on the ability of isatol and dimethylisatol to form well crystd. HCl salts. Below are given, resp., the values calcd. for the absorption of 1 mol. HCl and those found, and the characteristics of the resulting HCl salts: Dimethylisatin I (true dimethylisatin), 17.24, 0, no change; dimethylisatin II (supposed enol, dimethylisatinol), 17.24, 18.9, deep red crystals; dimethylisatin III (dimethylisatol), 17.24, 17.3, deep red crystals; dimethylisatin III Me ether, 16.03, 16.66, deep red crystals; dimethylisatin IV (dimethylisatinone), 17.24, 24.9 (?), blue-black soln. in HCl, giving much of a yellow salt; Me ether from dimethylisatin IV (dimethylisatinol Me ether), 16.03, 15.6. Only the dimethylisatin III, therefore, added exactly 1 mol. HCl, and even that must have been impure, for the resulting HCl salt was red while the pure salt is yellow. Similarly, the other prepns. must have been impure. In connection with the indophenin reaction it is pointed out that the indications it affords are not so unambiguous that it can be used under all circumstances for the characterization of isomers in the isatin series. The shade of the color produced depends greatly on the way the reaction is carried out. If only a very small amt. of a normal isatin, its *N*- or *O*-deriv. or a substitution product (0.0001 g.) in a few cc. of C_6H_6 containing thiophene is treated with concd. H_2SO_4 the acid becomes only red or at most red-brown; the so-called typical blue color occurs only when more of the substance is used and most distinctly when at least 0.001 g. of the substance in warm C_6H_6 is treated at once with the acid and allowed to stand some time if necessary. All isatols, on the other hand, give only a red-brown color. If the substances are not quite pure, the reaction may fail even when pure isatin derivs. are present if isatols and other non-defined impurities are also present. *Isatin 3,3-dichloride*, from 5 g. isatin in 10 cc. C_6H_6 and 10 g. PCl_5 allowed to stand, loosely stoppered, for 12 hrs. with frequent shaking, drained, washed with ligroin, alc. and H_2O pressed on clay and crystd. from C_6H_6 and charcoal, light yellow prisms, m. 165° (decompn.), gives in alc. with $PhNHNH_2.AcOH$ the yellow isatin β-phenylhydrazone, m. 210°. *N*-Me ether, similarly obtained from either II or the ether of III, yellowish prismatic crystals, m. 143°. To see if isatol chloride, isomeric with the known isatin chloride, might be obtained by elimination of HCl from the above dichloride, the latter was heated at 100° to const. wt. (11 hrs.); although the loss in wt. (18.9%) was approx. that calcd. for 1 mol. HCl (18.1%) the product on crystn. from C_6H_6 yielded a considerable amt. of the unchanged dichloride and no monochloride. Likewise the dichloride dissolves in concd. H_2SO_4 at 40° with evolution of HCl, which, however, is complete only at 60° but on dissolving the viscous mass in H_2O and extg. with Et_2O the latter yields only isatin. Isatol reacts with PCl_5 only in $POCl_3$, the yellow soln. becoming almost colorless in 24 hrs. When poured off from the excess of PCl_5 and freed from the $POCl_3$ as completely as possible *in vacuo* it deposits a small amt. of crystals stable towards H_2O and probably consisting of the expected isatol chloride but changing, as well as the non-cryst. residue, in the air and on long standing in a desiccator into a blue-green dye; alc. also instantly converts the colorless chloride into the blue-green dye, which is best obtained by evapg. the alc., taking up in alkali and adding acid; it seps. in dark blue-green, almost black crystals. C. A. R.

Constitution of the salts of isatin and related substances. A. HANTZSCH. *Ber.* **54B**, 1257–67(1921); cf. preceding abstr.—The views of Heller that there are two structurally isomeric Ag salts of isatin (I and II) and that the violet alkali salts are also *N*-salts of the type II, and also that dioxindol first forms violet *N*-salts analogous to the dark



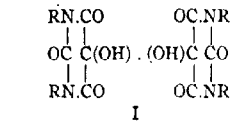
I II

violet isatin salts, which then rearrange into the known colorless *O*-salts, are so contrary to the results obtained by Hantzsch in his long investigations on numerous tautomeric compds. that Hantzsch has gone over the observations on which Heller bases his conclusions and as a result is convinced that the latter is mistaken. Practically no new exptl. material is given in the present paper. According to Heller, that "the imide H of isatin is the most strongly acid" is proved by the relatively strong acidity of free isatin as shown in its ability to decomp. AgOAc with formation of *N*-Ag isatin. As a matter of fact isatin is practically a non-electrolyte and, therefore, an infinitely weak acid as compared with AcOH, and secondly such pptn. reactions do not depend upon the relative strengths of the acids but upon the solubilities of the salts. Neither was it possible to confirm the alleged differences in color between the so-called *N*-Ag salt obtained from free isatin and the *O*-salt obtained from Na isatin, any more than the alleged differences in their behavior towards concd. NH_4OH on the one hand and C_5H_5N on the other. After repeated and variously modified expts. it has been established that perfectly pure Ag isatin can be obtained with certainty only when all alkalinity is avoided in the pptg. liquids, best by adding hot aq. AgOAc to aq. alc. isatin; the Ag isatin seps. in 75% yield while the rest remains dissolved in the AcOH set free. So obtained, the salt is Bordeaux-red, sol. in C_5H_5N with violet color, reacts very well with pure MeI after washing with H_2O, alc. and Et_2O and forms primarily the *O*-ether. But when instead of AgOAc is used a mixt. of $AgNO_3$ and NaOAc solns., especially when the latter is present in even very slight excess, the pptd. salt often has a brown color, which may even become almost black with an excess of NaOAc. This deepening in color, is due, however, not to an isomeric *N*-salt but to varying amts. of Ag_2O. Again, contrary to Heller's belief, aq. dioxindol treated with dil. bases gives at first *colorless* salts which *then* change, not by isomerization but by oxidation, into the violet salts of the primary oxidation product of dioxindol, the so-called isatyde, an addition product of isatin and dioxindol analogous to alloxantin, the addition product of alloxan and dialuric acid (see following abstr.). This can be shown as follows: colorless dioxindol dissolves, when protected from the air, in boiled out alkalies and $Ba(OH)_2$ without color and only when exposed to the air do the solns. become violet at the surface; the colorless soln. of isatyde in C_5H_5N is at once colored intensely violet by air-free $Ba(OH)_2$ and then deposits the insol. Ba salt of the same color while under these conditions dioxindol yields the colorless Ba salt. CHAS. A. ROUILLER

Tervalent carbon as chromophore in the halochromism of alloxantins and related substances. A. HANTZSCH. *Ber.* **54B**, 1267–79(1921).—One of the longest known and most striking cases of halochromism is that shown in the formation of salts by the colorless alloxantin which is at once pptd. by $Ba(OH)_2$ as the blue-violet insol. Ba salt. A similar behavior is shown not only by the *N*-Me derivs. of alloxantin, up to the tetra-Me deriv. (the so-called amalic acid), but by isatyde and hydrindantin, which are analogous to alloxantin, the primary reduction product of alloxan, in that they are the primary reduction products of isatin and indantrione. As to the nature of these deeply colored salts there exists more uncertainty even than as to that of the colorless mother substances. As they are very unstable their empirical compn. had not yet been detd. and in fact it had not been settled whether they are really derived

from the unchanged alloxantins or perhaps from one of their decompn. products (cf. Ruhemann, *C. A.* **5**, 3565). H., however, has succeeded in showing definitely that they are direct derivs. of alloxantin, for he was able to prep. from all the alloxantins different analytically pure Ba and alkali salts which on cautious acidification smoothly regenerated the original alloxantins and not the dialuric acids formed secondarily from them by oxidation. The violet salts from alloxantin and sym. and asym. dimethylalloxantins contain 4 atoms alkali or 2 atoms of Ba per mol. of alloxantin, those from amalic acid 2 atoms alkali or 1 atom Ba. The alkali salts dissolve in H_2O with almost instant decolorization and decompn. into dialurates and alloxanates, and can, therefore, be prepd. only in alc. soln. The alk. earth salts (especially Ba) are, on account of their insoly., more stable and can, therefore, be kept under the pptg. fluid but are decompd. like the alkali salts on washing with H_2O, only more slowly, and rapidly by CO_2; if they are treated immediately after their prepn. with moderately concd. acids the resulting colorless insol. residues show the m. ps. of the corresponding alloxantins; the ppts. obtained with dil. acids or on acidification of solns. almost always have indefinite m. ps. as under these conditions the alloxantins and especially their salts easily undergo oxidation and cleavage into their components. In this way were prepd. the deep violet amorphous *barium alloxantin*, $C_8H_2O_8N_4Ba$ (Ba, 49.63%; calcd., 49.34), from aq. alloxantin quickly mixed with excess of $Ba(OH)_2$; *sodium*, *potassium* and *rubidium salts*, blue-violet amorphous ppts. from alloxantin in abs. alc. and 0.1 *N* alcoholate; *barium amalate*, $C_{12}H_{12}O_8N_4Ba$, violet mass from the finely powdered tetramethylalloxantin shaken several hrs., protected from CO_2 and O, with excess of $Ba(OH)_2$. That Ruhemann's blue salts are derived from hydrindantin, corresponding to alloxantin, and not from dioxindone, corresponding to dialuric acid, is indicated by the fact that when hydrindantin, which is difficultly sol. in H_2O, is dissolved in C_5H_5N and immediately treated with freshly boiled out $Ba(OH)_2$ there is immediately and quant. pptd. a deep blue salt from which hydrindantin is regenerated on treatment with acids. The compn. of these salts indicates that the pinacol-like formulas (I, II and III) originally assigned to alloxantin, hydrindantin and isatyde are more probably the correct ones and their correctness may be considered as proved if they can explain the two most striking peculiarities of these substances: (1) the easy formation and the equally easy rupture of the simple C union, and (2) the chem. changes in the halochromism. For the latter must also be detd. which atomic groups are essential for the formation of the chromophore of the salt. The urea, C_2H_6 and NH_3 residues, resp., are not essential, but of importance is the group $=C(OH).CO-$ common to the three types of compds. and also very probably the second negative residue bound directly to the C(OH) group (CO in the case of the alloxantins and hydrindantins, C_6H_4 in that of the isatydes), so that in the salt formation the chromophore must be produced by a chem. change within the complex IV or V. The salt formation by weak acids is accompanied by a chem. change whereby the strongly positive metals replacing the H of the HO become "ionogenic," *i. e.*, are bound to both O atoms in salts containing a HO and a CO group. But in the case of the above compds., this not very great change in constitution does not suffice to account for the anomalously great optical change in the halochromism (from colorless to blue-violet). Moreover, in the alloxantin series in the formation of the monometallic salts, where the change from the non-ionogenic to the ionogenic union occurs in only half of the mol., as in Behrend's colorless Ba salt (VI) of benzoylalloxantin, there is no optical change visible to the eye and only when the Bz group is split off is the violet-blue di-Ba salt formed. The only possible way of explaining this very great optical change by a corresponding radical chem. change in the above complexes is by assuming a rupture of the union, in itself very loose, between the two central C atoms, *i. e.*, a halving of the mol. and the formation of tervalent C as the essential constituent of the

chromophoric complex of the violet salts, which are, therefore, closely related to Schlenk's blue metal ketyls. That the colored salts from hydrindantin can also be formed only through the production of a tervalent C atom can be shown as follows: If hydrindantin is heated to boiling with an amt. of anhydrous C_5H_5N insufficient for soln. the originally yellowish soln. becomes deep bluish red and on cooling deposits hydrindantin and again becomes almost colorless, a phenomenon which can be explained only by assuming that the hydrindantin (even if only in small amt.), as a C_5H_5N solvate, decomps. at the higher temp. into two equal halves with tervalent C which, being more strongly acid, form a salt with the C_5H_5N.



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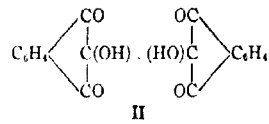

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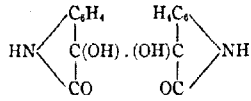

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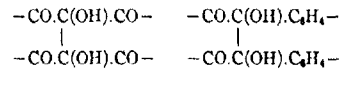

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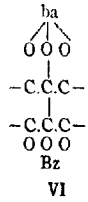
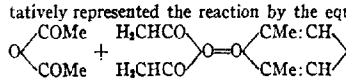


VI

CHAS. A. ROUILLER

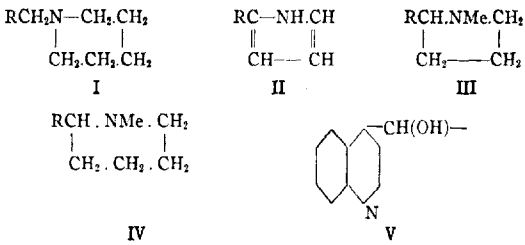
Reaction mechanism of the Skraup-Priglinger dimethylpyrone synthesis. ERNST PHILLIPPI AND REINHARD SEKA. Univ. Wien. *Ber.* **54B**, 1089–91(1921).—S. and P., who found that dimethylpyrone (A) is always formed in about 2% yield when Ac_2O is boiled some hrs. under a reflux with concd. H_2SO_4 (Kremann, *C. A.* **4**, 2404), tentatively represented the reaction by the equation



If their view is correct, the addition of Me_2CO should facilitate the reaction and the use of higher ketones instead of Me_2CO should give higher homologs of A. Such has been found to be the case. Thus, in the presence of Me_2CO the yield of A is increased to 4%. The S.-P. method was further slightly modified as follows: 5.8 g. Me_2CO and 30.6 g. Ac_2O in ice-salt are treated dropwise with 7 cc. H_2SO_4, and secondly, the vacuum distn. is stopped at the instant when heavy white vapors begin to be evolved. 2,3,6-Trimethylpyrone, m. 78°, was obtained from 120 g. Ac_2O and 29 g. MeCOEt allowed to stand some hrs. with 24 cc. concd. H_2SO_4, then boiled 4 hrs. under a reflux, freed from the AcOH by distn. *in vacuo*, taken up with satd. $(NH_4)_2SO_4$, filtered, made slightly alk. with NH_4OH and repeatedly extd. with C_6H_6; it was identified by conversion into the 4-pyridone by heating 8 hrs. at 100° in H_2O satd. with NH_3. CHAS. A. ROUILLER

Synthesis in the quinine series. II. Compounds resembling quinine. L. RUZICKA. *Helvetica Chim. Acta* **4**, 482–5(1921); cf. *C. A.* **13**, 3179.—The synthesis of β-collidine (*C. A.* **13**, 3179) is the last step in the series of reactions which makes possible

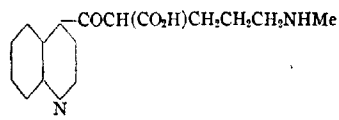
the complete synthesis of the dihydroquinine alkaloids, and to complete the synthesis, König's homocincholoipine (*C. A.* **14**, 1980) must be resolved into its active components. The present investigation is undertaken to confirm the constitutional formula of these compds. Kaufmann (*C. A.* **7**, 2938) and Rabe, Posternack and Kindler (*C. A.* **11**, 2790) have obtained compds. of the type **I** (R = **V**) and Karrer (*C. A.* **12**, 1290) of the type **II**. These compds. do not contain the characteristic quinuclidine ring. In compds. of type I the C atom between the N and the C bearing the OH group is not a member of a ring as is the case in the quinine compds. The type **II** fulfils this condition but the aromatic nature of the pyrrole ring does not render it equiv. to the quinuclidine ring. The compds. of the types **III** and **IV** resemble the quinine alkaloids in respect to these 2 characteristics, *viz.*, hydrogenated system with strong basic properties as well as having direct ring connection of the carbon which joins the N and the C bearing the OH group. These compds. are designated monocyclic cinchona alkaloids in contrast to the bicyclic naturally occurring compds., and the synthesis of the aliphatic quinatoxines, from which



these monocyclic compds. may be derived, is described in the following abst. **III. Aliphatic quinatoxines.** *Ibid* 486–505.—Et cinchoninate (**A**) was condensed with *N*-methylpiperidone (**B**) (the lactam of $MeNH(CH_2)_4CO_2H$) by means of NaOEt and this product was sapond. with HCl into the unstable ketonic acid (**I**) which with loss of CO_2 gave the aliphatic quinatoxine, quinolyl δ-methylaminobutyl ketone. This reaction is a modification of the acetoacetic ester condensation, alc. splitting out from the ester group with a H atom from a reactive CH_2 group. Other examples of this condensation in the case of compds. resembling acid amides are not known. Et α′-methoxypyridine-β-carboxylate did not react with **B**. Weidel (*Monatsh.* **17**, 401 (1896)) prepd. acetoacetylquinoline from Me_2CO and **A**. Pinner (*Ber.* **34**, 4234 (1901)) prepd. compds. of the type **II** by condensing pyridinecarboxylic ester with fatty acid esters. Rabe and Posternack (*C. A.* **7**, 2553) used this reaction for the synthesis of γ-quinolylacetic ester, $C_9H_8NCOCH_2CO_2R$, and Rabe and Kindler (*C. A.* **13**, 716) for the prepn. of cinchona toxines. The condensation of **A** and **B** was effected with dry NaOEt in C_6H_6 and its homologs as well as in petr. ether. At ordinary temp. in 24 hrs. a 50% yield of the condensation product was obtained and the yield remained const. in spite of heating for several days. An excess of 1.33 mols. NaOEt was found to be beneficial. 145 g. **A** and 81.5 g. **B** in 200 cc. low boiling petr. ether were shaken with 70 g. powdered NaOEt. After refluxing for 12 hrs. the reaction mixt. was treated with cold H_2O, the ether was removed from the clear soln. and most of the alkali was neutralized (ice) with glacial AcOH and when the clear soln. was treated with CO_2 the condensation product sepd. (60% of the theory), γ-quinolyl β-*N*-methyl-α-piperidonyl ketone (**C**), monoclinic prisms from ether, m. 95°, a white powder, which in concd. alc. soln. gives with $FeCl_3$ a dark almost black color, which is violet in great diln. Excess of **B** in the mother liquors can be recovered by exhaustive extn. with ether. **C** gives in alc. a crvst. ppt. of the *picrate*, m. 207° (decompn.), whereas the picrates of the trans-

formation product are flocculent and amorphous. **C** when warmed 2 days with 25% HCl in sealed tubes at 100° still showed the color reaction with $FeCl_3$. This color reaction could not be obtained after heating for 3 hrs. with concd. HCl at 120–30°. The excess of HCl was removed by heating *in vacuo*, Na_2CO_3 was added and the oil which sepd. was taken up in ether, dried with KOH and when the ether was evapd. a thick brown oil, γ-quinolyl δ-methylaminobutyl ketone (**D**), was formed in theoretical yield. Resinification resulted on standing in thin layers in the air, and sealed specimens solidified almost completely within 1 yr. **D** is sol. in ether but no crystals were obtained. The *dipicrolonate*, m. 160°, was prepd. by pouring a concd. alc. soln. of the ketone into satd. alc. picrolonic acid. The additive compds. with picric acid and trinitroresorcinol were not easily crystd. The *dihydrochloride* prepd. by dissolving the ketone in 2 mols. HCl, m. 171–2° in closed tubes. 70 g. **D** in 200 cc. 40% HBr at 50° while being well stirred were treated with 50 g. Br vapor and from the clear soln. (clear when care be taken) HBr was driven off at 40°. The residue yielded 100 g. γ-quinolyl δ-methylbromoaminobutyl ketone dihydrobromide (**E**), m. 149°. **E** in ice H_2O was shaken with an excess of KOH and extd. several times with ether. The ext. dried with KOH gave *in vacuo* a yellow-red thick oil which was extremely unstable and on heating gently or on long standing became ether-insol. The ether soln. was treated with 1 mol. HCl in dil. soln. and *γ-quinolyl α-N-methylpyrrolidyl ketone hydrochloride* (**F**) was obtained as a red-violet residue by evapn. *in vacuo* with gentle heat., crystals from hot alc. m. 180°. The yield of **F** was increased when the use of H_2O was avoided, and the reaction was carried out in alc., 27 g. **A** and 17 g. *N*-ethyl-α-piperidone (**G**) were condensed with 13 g. NaOEt as in the case of **B**. CO_2 treatment followed by ether extn. gave 24 g. noncryst. *γ-quinolyl β-N-ethyl-α-piperidonyl ketone* (**H**) (63% yield). The *picrate*, yellow ppt. from alc. m. 223–5° (decompn.). **H** was heated during 2 days with 7 times its wt. of concd. HCl and the residue obtained *in vacuo* at 100° was the *dihydrochloride* (**I**), colorless hygroscopic powder, m. 166–7°, from alc. When **I** was treated with aq. NaOH the ketone formed was taken up in ether, but after long standing no crystals were obtained, consequently the *dipicrolonate*, yellow-brown crystals from alc., m. 165°, (decompn.) was prepd. On bromination it yielded *γ-quinolyl δ-ethylbromoaminobutyl ketone dihydrobromide*, crystals, m. 161–2° (decompn.). 157 g. Et quininate and 77 g. **B** in 400 cc. petr. ether were heated 24 hrs. with 61 g. NaOEt. The brown solid cake was digested with dil. AcOH and the condensation product sepd. as a flocculent ppt. which was filtered after satn. with $NaHCO_3$. A 50% yield or 105 g. of γ-*p*-methoxyquinolyl β-*N*-methyl-α-piperidonyl ketone (**K**), transparent colorless prisms, m. 125–6°, was obtained. The *hydrochloride* is slightly sol. in H_2O and the *picrate*, yellow needles from alc., m. 212–3°. **K** was sapond. with HCl and after the excess of HCl was drawn off *in vacuo* NaOH (not Na_2CO_3) was added and the ketone which sepd. was taken up in ether. CO_2 when added to the alk. soln. caused sepn. of a compd. which was not investigated. The methoxyketone is a thick yellow oil, which would not cryst. and with picric acid and trinitroresorcinol no stable compds. were formed. The *dipicrolonate*, a yellow cryst. powder, m. 212–4°. The *dihydrochloride* was prepd. by treating the ketone with 2 mols. HCl and after vacuum evapn. the tarry mass was taken up in alc. and canary-yellow needles m. 167–8° were obtained. γ-*p*-Methoxyquinolyl δ-methylbromoaminobutyl ketone dihydrobromide, m. 134–5°, was obtained by adding Br as in the case of the other ketone. 130 g. **A** and 75 g. cyclohexanone isoxime (**L**) and 88 g. NaOEt were heated in 300 cc. C_6H_6 for 2 days and the product in 3 l. of aq. ext. gave when treated with CO_2 40 g. of brown condensation product. When C_6H_6 or petr. ether was used at 100° similar results were obtained. The **L** which did not react was regenerated, although a part of it was decompd. by heating with NaOEt. Only 0.5 of the condensation product could be extd. with ether, but the residue is sol.

in $CHCl_3$ and both products gave red colors with $FeCl_3$. Picric acid and trinitroresorcinol did not yield cryst. solids from alc. but *γ-quinolyl 3,2-ketohexamethylene-1-imino ketone picrolonate*, of the ether-sol. portion, m. 130° from alc., a yellow powder and the *picrolonate* (**M**) of the ether-insol. fraction m. 190°. When **M** was heated with concd. HCl in a stream of CO_2, the HCl drawn off, alkali was added, and extd. with ether, it gave 6 g. oil. The chief portion of the reaction product is insol. in ether, but is sol. in $CHCl_3$. Both portions gave γ-quinolyl ε-aminopentyl ketone *dipicrolonate*, yellow powder from alc., m. 206–7° (decompn.), and the same *dihydrochloride* (**O**), m. 206°, with excess alc. HCl. 7 g. **A** and 8.5 g. benzoylcyclohexanone isoxime in C_6H_6 were heated for 24 hrs., with 3.1 g. NaOEt, H_2O was added, the C_6H_6 was sepd. and when CO_2 was passed into the soln. *γ-quinolyl-3,2-ketohexamethylene-1-benzoylimino ketone* (**N**) was formed. This compd. gave a violet color with $FeCl_3$ and with picric acid and trinitroresorcinol sol. products were obtained but the *dipicrolonate* (not analyzed) was rather difficultly sol. When **N** was hydrolyzed with 20% HCl in sealed tubes at 130° for 2 days and the HCl drawn off, alkali caused the formation of **O** (mixed m. p., 206°). 55 g. **A** and 70 g. **L** were heated 1 day with 325 g. NaOEt in petr. ether. Alkali, AcOH and CO_2 treatment gave a rather sol. condensation product which was extd. with ether. The ext. was dried with $MgSO_4$, unchanged **L** was removed by low boiling petr. ether and the product, γ-quinolyl 3,2-ketohexamethylene-1-methylimino ketone (**P**), crystals from AcOEt, m. 151–2°. This compd. gave with $FeCl_3$ in alc. a green color. When **P** was sapond. with HCl, *γ-quinolyl methylaminopentyl ketone*, a thick brown oil, resulted, the hydrochloride and picrate of which were unstable, but the dipicrolonate m. 195° from alc. and the *distyphnate*, from alc., m. 198°. When **P** was treated during one day with HCl in a stream of CO_2, and evapd., the yellow residue gave a hygroscopic *dihydrochloride*, m. 179–80° (decompn.) in sealed tube. Me α-methoxynicotinate (Meyer, *Monatsh.* **28**, 59(1907)) was prepd. by treating Me α-chloronicotinate with NaOMe in sealed tubes. Pechmann (*Ber.* **17**, 2395(1884)) prepd. the free acid by treating cumalic ester with $MeNH_2$ followed by sapon. 100 g. malic acid were warmed on the water bath with 300 g. of a mixt. of equal parts concd. and fuming H_2SO_4 with 18% SO_3. The mass was heated to 100° with abs. alc. on the water bath, poured on to ice, neutralized with Na_2CO_3 until NaCl sepd. and then ether-extd. 150 g. ethyl cumalate, b_{12} 140–2°, m. 36°, were obtained from the $CaCl_2$, treated ext., and when the $MeNH_2$ from 125 g. $NHMe_2HCl$ in 300 cc. alc. were added during 2 hrs. to 140 g. of the ester in 100 cc. alc. *ethyl α'-methoxynicotinate*, prisms from alc. m. 71°, $b_{0.25}$ 135°, was formed. H. E. WILLIAMS



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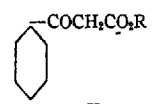


II

Cinchona alkaloids. IV. Transformations of the diazonium compounds of 5-aminocupreine and of 5-aminohydrocupreine and their methyl and ethyl ethers. Formation of diazo anhydrides and of cuprean and hydrocuprean and their ethers. β-Ethylcupreine. G. GIEMSA AND J. HALBERKANN. Inst. Schiffs- u. Tropenkrankheiten, Hamburg. *Ber.* **54B**, 1167–89(1921); cf. *C. A.* **14**, 3235.—When the diazo solns. of the ethers of the 5-hydroxycinchona alkaloids, which immediately after their prepn. couple normally in soda with β-naphthol to red azo dyes, are allowed to stand, the coupling power of the acid solns. disappears completely without any evolution of N and if they are now made alk. with soda or NaOH there seps. a yellowish ppt. crystg. from Et_2O in golden yellow leaves or needles, sensitive to light but stable in the dark and away from

the air, deflagrating on rapid heating on Pt foil and gradually decompg. on slow heating. Both ethers, as well as the free phenol in both the cupreine and the hydrocupreine series, yield the same compd., which is a diazo anhydride. That such an anhydride should be formed from the aminophenols can readily be understood from the structures of the latter, but the sapon. of the ethers (which occurs on mere standing of the acid diazo solns. in the cold), making possible the formation of the anhydride, is peculiar and only a few cases of a similar kind are known. A similar reaction occurs, but to a much less marked degree, with a simpler *o*-aminophenol ether (*o*-$MeOC_6H_4NH_2$). The solns. of the anhydride couple with β-naphthol neither in acid nor in alk. soln. nor with other simple phenols. Even with more reactive phenols in AcOH azo dyes are formed only very slowly and can be detected only by their spectroscopic behavior; α-naphthol and pyrogallol do not react at all, resorcinol and orcinol only very little, phloroglucinol somewhat more, but coupling occurs immediately in alc. alk. soln. The coupling occurs only in the *p*-position and when there is a second phenol group in the *m*-position. Even when no reducing agent is added the anhydride, on heating either in dil. acids or in alkalies, quant. loses the diazo N as such and the diazo group is replaced by H, the sec. alc. likewise being reduced to the hydrocarbon. Since the resulting phenols are probably closely related to quinene they are designated *cuprean* and *hydrocuprean*. No clear explanation of the mechanism of this reduction can be given. Before the existence of the anhydrides had been discovered it was suggested that the double reduction might be an intramol. process, induced by the alc. split off, which itself was converted into the aldehyde or acid. Expts., especially with aminohydroquinine, however, gave no indications of the formation of HCHO or HCO_2H; the CO_2 observed could have owed its formation only to a side reaction; moreover, MeOH (33% of the calcd. amt.) was recovered in the distillate. Moreover, the same cuprean and hydrocuprean are obtained not only from the diazotized aminophenols but also from the corresponding anhydrides, which cannot split off alc. That the O is not attached to N and split off as N_2O or NO was also established. The only possible explanation that remains is that there simultaneously occurs an oxidation of a part of the substance, although there is no evidence for this other than the small yield of the phenols (40%). That the anhydrides are more stable establishes that these are the first products when the diazo solns. are boiled and that their formation precedes the reduction. Under different conditions the process in the case of the ethers can be reversed, so that the reduction becomes the primary reaction. If the diazo soln. of the ether is stirred with Cu paste immediately after its prepn. N is evolved and the diazo and alc. groups are reduced but the ether group remains intact and on hydrolysis with HCl under pressure is obtained the phenol, and inversely the ethers obtained with Cu paste can be prepd. by alkylation of the phenols. G. and H. do not feel they can adopt the nomenclature proposed by Heidelberger and Jacobs (*C. A.* **14**, 544) (the abstr. of whose paper came to their attention only after their own work had been completed) for the desoxy derivs. of the cinchona alkaloids. To 5 g. aminoethylhydrocupreine in 85 cc. *N* H_2SO_4 at 0° is added 25 cc. of 4 % $NaNO_2$, then 100 g. H_2SO_4 (d. 1.4) and 50 g. dehydrated Na_2SO_4, and the mixt. is heated 1.25 hrs. at 85–90°, almost neutralized in ice with NaOH, treated with 2 g. $Na_2S_2O_4$ in a little H_2O, made alk. after a few min. with NaOH, shaken with $CHCl_3$, treated with CO_2 or acid and soda and exhaustively extd. with much Et_2O. The combined exts. are washed a few times with H_2O, dried, boiled a long time with charcoal and concd., whereupon the *hydrocuprean* (A), $C_{19}H_{24}O_2N_2$, seps.; it crysts. from $CHCl_3$-Et_2O in bitter rectangular leaves or tables, m. 173°, easily sol. in dil. acids, alkalies, $PhNH_2$, alcs., $PhNO_2$ and $CHCl_3$, insol. in H_2O, soda and petr. ether, stable in the air when dry but easily becomes reddish when moist, forms a non-fluorescent soln. in HNO_2, gives at most a faint greenish color in the thalleioquin reaction, instantly reduces $KMnO_4$ in H_2SO_4, gives no color with $FeCl_3$

in H_2O, a red color in concd. alc. soln. and a more brown color in dil. soln., forms an olive-gray ring when stratified in NaOH with dil. Br water and on shaking and adding more Br forms a faint green soln. with green fluorescence which disappears on acidification; H_2SO_4 (d. 1.84) forms a colorless soln. with greenish blue fluorescence. A shows $[\alpha]_D^{20}$ 90.0° (abs. alc., *c* 0.8666), 97.5° (Et_2O, *c* 0.2194), seps. from dil. alc. or Me_2CO in stout prisms with 1 H_2O, m. 134° and (anhydrous) 172°, is not reduced by H and Pd, mol. wt. in freezing $PhNO_2$ 818, in freezing $PhNH_2$ 307, in boiling $CHCl_3$ 410, in freezing $C_{10}H_8$ 665, by titration with litmus 286. *Dihydrochloride*, hexangular leaflets on rapid, stout quadrangular columns on slower crystn. from EtOH-Et_2O, sinters 185°, m. 191–2°. *Chloroplatinate*, triangular leaflets from concd. HCl, begins to decomp. 290°. Aminohydroquinine gives the same compd. **A**; in decompg. the diazo compd. from 20 g. of the base, in which the H_2SO_4 and Na_2SO_4 were omitted, the evolved gases were carried by means of a current of N through an empty U-tube in a freezing mixt., then through H_2O at 0° and finally through two $Ba(OH)_2$ wash bottles. Among the products so obtained were identified 0.71 g. MeOH (calcd., 2.36), 0.063 g. CO_2 (calcd. for complete oxidation of the Me group, 2.59 g.) and traces of HNO_2; HCN, HCHO or HCO_2H could not be detected. Aminohydrocupreine gives the same phenol but in poorer yield as, owing to the proximity of the free phenol group, the NH_2 group is not smoothly diazotized as in the case of the ethers; after addition of the calcd. amt. of $NaNO_2$ there persists a strong odor of HNO_2 and this reacts with a part of the base, as shown by the occurrence of side reactions and a greater formation of CO_2. All three of the above diazotized NH_2 compds. also give **A** when heated in H_2SO_4 with $CuSO_4$ at 60–5°; an odorless gas is evolved and there is formed a relatively large amt. of a brown powder very difficultly sol. in all org. solvents sepg. from AmOH-$C_{10}H_8$ in fine red-yellow microneedles or cubical crystals containing Cu, sol. in H_2SO_4 (d. 1.84) with brown-red color becoming violet-red on diln., decomps. about 350°. *Ethylhydrocuprean*, from 3.3 g. **A** in 33 cc. abs. alc. containing 0.5 g. Na heated 3 hrs. at 60° with 4.4 g. *p*-$MeC_6H_4SO_3Et$, 0.5 the same amts. of NaOEt and sulfonate being added after 2 hrs., dild. with H_2O, freed from alc. and unchanged ester, made alk., extd. with Et_2O, evapd., taken up in acid, again extd. from alk. soln. with Et_2O, evapd. and boiled with charcoal in petr. ether, viscous oil (2.2 g.), gives an intense green color with Br water-NH_4OH, is stable towards $KMnO_4$ in H_2SO_4, shows in H_2O containing HNO_2 azure to blue-green fluorescence, is very bitter, does not give with NaOH and Br water the reactions of the phenol **A**, $[\alpha]_D^{20}$ 77.7° (alc., *c* 0.8496), 77.8° (Et_2O, *c* 0.9124), mol. wt. in freezing C_6H_6 320; *chloroplatinate*, reddish yellow powder of microspheres, begins to carbonize about 250°. The ether (2 g.) heated 8 hrs. at 145° with 10 cc. HCl yields EtCl and **A**. *Methylhydrocuprean* (*hydroquinan*) is obtained only in small amts. on methylation with Me_2SO_4 or $MeC_6H_4SO_3Me$ but is smoothly formed with CH_2N_2 in Et_2O added to **A** in AmOH at 0°; it is an oil with properties like those of the Et ester, $[\alpha]_D^{20}$ 81.7° (alc., *c* 1.1016); it can be obtained directly from aminohydroquinine by immediately treating the diazo soln. in ice with an equal part of moist Cu paste, stirring for some time longer after the evolution of gas has ceased, treating with talcum, filtering, shaking the acid soln. with Et_2O, making alk. with NaOH, extg. with Et_2O, evapg. and boiling in petr. ether with charcoal; yield, 50%. The Et ester (see above) can in the same way be obtained directly from diazotized aminoethylhydrocupreine by means of Cu paste. The diazotized soln. of aminoethylhydrocupreine loses its power to couple with β-naphthol on standing, sometimes in 10 min. if the more or less acid soln. is highly evacuated; the anhydride formation occurs instantly on addition of alkali. Soda or NaOH produces a yellowish white amorphous ppt. of the *hydrocupreine-5-diazo anhydride* (**B**), $C_{19}H_{22}O_2N_4$, bitter, brownish yellow to golden yellow, slender, triangular leaflets from ether (yield, 65–70%), sensitive to light, especially when moist, becoming more and more brown,

but stable in the dark in a desiccator, easily sol. in acids, alcs. and $CHCl_3$, moderately in Me_2CO and C_6H_6, difficultly in AcOEt and CS_2, very slightly in Et_2O (1:3000), insol. in H_2O, alkalies and petr. ether; alc. solns., especially when dil., are not stable, soon turning green and then slowly red; ammoniacal alc. solns. quickly become green, then violet-red; dissolved in a little acid, then treated with excess of NaOH and with Br water it gives a characteristic fuchsin-like red color which gradually disappears and under the proper conditions leaves a yellow-green color; characteristic, also, is the currant-red color produced, together with vigorous evolution of N, by adding a trace of $(NH_4)_2S$ to an alc. soln.; it does not fluoresce in dil. HNO_3; in the thalleioquin test Br water alone produces a faint green color which is not increased by NH_4OH although the latter produces a green-blue fluorescence; the soln. in dil. H_2SO_4 is yellow, in concd. acid (d. 1.84) colorless; $FeCl_3$ gives no color in H_2O or alc.; **B** deflagrates on rapid, slowly decomps. on slow, heating, beginning to darken 120°, suddenly becoming deep dark brown-red at 143–5°, then slowly dark violet-red, carbonizes above 200°, $[\alpha]_D^{20}$ 92.4° (alc., *c* 0.6384), −23.9° (Et_2O, *c* 0.0732). **B** is also obtained in 72–5% yield from aminohydroquinine and in much smaller yield (about 30%) from aminohydrocupreine. *Dihydrochloride*, light yellowish, long, quadrangular needles from $CHCl_3$-EtOH-Et_2O. **B** yields **A** when heated in 5–10% H_2SO_4 at 90°, also when the soln. in abs. alc. and 0.5 g. H_2SO_4 (d. 1.84) is concd. in a current of CO_2, and when attempts are made to reduce it catalytically (Ni in H_2SO_4 or Pd in alc.); with Ni $^1/_8$ mol. H_2 is absorbed after shaking 2 hrs., while with Pd there is even a slight increase in vol. (4.4 cc. for 1 g. **B**); if the change to **A** were a purely intramol. process the vol. should be increased 66.2 cc. by the N evolved, so that absorption of H must take place but is replaced by approx. the same amt. of liberated N. *Cupreine-5-diazo anhydride*, $C_{19}H_{20}O_2N_4$, obtained in 34% yield, golden yellow leaflets from Et_2O, begins to turn brown above 120°, suddenly becomes dark violet-red at 145–6° and gradually carbonizes at higher temps., is sol. in about 1400 parts Et_2O, $[\alpha]_D^{20}$ 89.5° (alc., *c* 0.8380), −19.3° (Et_2O, *c* 0.0724), also obtained from aminoquinine and its Et ether and decomps. on heating in dil. acids into N and *cuprean*, $C_{19}H_{22}ON_2$, which is prepd. by heating diazotized aminocupreine or its ether with $CuSO_4$ or Na_2SO_4 for some time at 80–5° or better by dropping a 5% H_2SO_4 soln. of the anhydride into the same amt. of boiling H_2O; it seps. from C_6H_6 in stout needles, m. 206°, easily sol. in NaOH, acids, alcs., $CHCl_3$, difficultly in Me_2CO, Et_2O and C_6H_6, insol. in H_2O, soda and petr. ether, does not fluoresce, gives only an indication of the thalleioquin reaction, is instantly attacked by $KMnO_4$ in H_2SO_4, gives the same reaction as **A** with Br water in NaOH, is practically tasteless but forms very bitter acid salts, $[\alpha]_D^{20}$ 82.8° (alc., *c* 1.0144). *Methylcuprean (quinan)*, obtained only in small amt. with Me_2SO_4 or *p*-$MeC_6H_4SO_3Me$ but smoothly from CH_2N_2 in Et_2O and the phenol in AmOH at 0°, oil which solidifies in the cold, insol. in H_2O and alkalies, shows greenish blue fluorescence in dil. HNO_3, gives a strong positive thalleioquin test, is unstable towards $KMnO_4$, $[\alpha]_D^{20}$ 70.1° (alc., *c* 1.3972). *Ethylcuprean*, prepd. with Et_2SO_4 or $MeC_6H_4SO_3Et$, yellowish oil solidifying in the cold, shows green-blue fluorescence in dil. HNO_3, $[\alpha]_D^{20}$ 66.5° (alc., *c* 0.8050). When 5 g. aminoethylcupreine in 85 cc. *N* H_2SO_4 is diazotized at 0° with 25.5 cc. of 4% $NaNO_2$ and at once stirred with 5 g. Cu paste, then, when the evolution of N has ceased, treated with talcum, filtered, made alk., extd. with Et_2O, evapd. and extd. with petr. ether, there is obtained a *β-ethylcupreine*, stout quadrangular columns from Et_2O-petr. ether, m. 164–5°, at once reduces $KMnO_4$, gives a strong positive thalleioquin reaction and blue-green fluorescence in HNO_3, $[\alpha]_D^{20}$ −52.8° (alc., *c* 0.8708), depresses the m. p. of the isomeric ethylcupreine (m. 165–6°) to 135°, converted by catalytic reduction with Ni and subsequent dealkylation with 5 parts HCl (d. 1.125) at 145°, not into the expected β-hydrocupreine but into **A. V. Stereoisomeric compounds of hydrocuprean.** *Ibid* 1189–204.—The hydrocuprean (**A**) de-

scribed above is, from its compn. and prepn., a hydrocupreine in which the sec. alc. has been reduced to the hydrocarbon. It might be identical with the phenol obtained from hydroquinine or its Et homologs by reduction and sapon. or by the same reactions in reverse order or it might be identical with the reduction and sapon. product of desoxyquinine or of desoxyquinidine. Expt. showed, however, that the latter phenols are stereoisomeric, not identical, with **A.** The reduction of hydroquinine could not be effected so it cannot be stated whether A is identical with the reduction and sapon. product of this compd. Quinine chloride, from quinine-HCl and PCl_5 in $CHCl_3$, contains no H_2O of crystn. as stated in Beilstein (III, 817), a statement already corrected by Rabe (*C. A.* **4**, 2136), $[\alpha]_D^{20}$ 62.6° (alc., *c* 2.1552). Quinene, prepd. by boiling the above chloride with alc. KOH, boiling out the resulting oil with benzine (b. 60–100°), cooling completely, pouring off from the undissolved material, rubbing the oil remaining on evapg. the soln. on ice until it solidifies and crystg. from 50% Me_2CO, quadrangular columns with 2 H_2O, m. 67°, solidifies on higher heating, m. again somewhat turbid 90–1°, $[\alpha]_D^{20}$ 52.5° (abs. alc., *c* 1.5892); dihydrochloride, fine long Cr-yellow needles, m. 182°. *Ethylcupreine chloride*, from ethylcupreine (obtained in 62% yield from cupreine and *p*-$MeC_6H_4SO_3Et$) in the form of the HCl salt and PCl_5 in $CHCl_3$, prisms, m. 130°, $[\alpha]_D^{20}$ 55.5°, 56.2° (alc., *c* 2.2892, 1.0404), converted by boiling with alc. KOH into *ethylcupreine*, yellowish oil from petr. ether, solidifies on cooling, gives a blue-green fluorescence in dil. HNO_3, instantly reduces $KMnO_4$ in H_2SO_4, gives a fine thalleioquin reaction, $[\alpha]_D^{20}$ 36.5° (alc., *c* 1.7384). *Cupreene*, from quinene heated 7 hrs. at 150° with 5 parts HCl (d. 1.125), could not be obtained in cryst. form, remains on evapn. of the Et_2O soln. as a varnish easily sol. in all org. solvents which shows no fluorescence in dil. HNO_3 and gives no thalleioquin reaction, immediately reduces $KMnO_4$ in H_2SO_4, sinters about 85°, m. around 110°, $[\alpha]_D^{20}$ 11.8° (alc., *c* 1.3130). Hydroquinine chloride, from hydroquinine (prepd. from quinine by catalytic reduction in H_2O with Ni) and PCl_5 in $CHCl_3$, quadrangular prisms, m. 144°, turns yellow in the light, does not reduce $KMnO_4$, gives a positive thalleioquin reaction, shows no fluorescence in dil. HNO_3, $[\alpha]_D^{20}$ 43.0° (alc., *c* 3.0136); its neutral salts form yellowish cold and yellow hot solns. *Hydroquinene*, prepd. like quinene, the Et_2O soln. of the product being boiled a long time with charcoal, filtered, concd., treated with 3 parts petr. ether and at once filtered from the resulting brown flocks, needles or hexangular columns with 2 H_2O from aq. Me_2CO, m. (anhydrous) 78–9°, fluoresces in HNO_3, instantly reduces $KMnO_4$, gives a beautiful green color in the thalleioquin reaction, $[\alpha]_D^{20}$ 29.5° (alc., *c* 2.6780); *dihydrochloride*, fine long deep yellow needles from the base in MeOH-AcOEt and HCl in Et_2O. *Ethylhydrocupreine chloride* (yield, 81%), quadrangular prismatic columns, m. 147°, turns yellow in the air, gives a weaker thalleioquin reaction than the mother base, does not fluoresce in HNO_3, dissolves easily in dil. acids with yellowish, in concd. H_2SO_4 with yellow color, $[\alpha]_D^{20}$ 37.7°, 37.2° (alc., *c* 0.8484, 2.6644). *Ethylhydrocupreene*, viscous yellowish oil, shows in HNO_3 green or at most bluish green fluorescence, gives a positive thalleioquin test, immediately decolorizes $KMnO_4$ in H_2SO_4, $[\alpha]_D^{20}$ 29.8° (alc., *c* 1.0916). *Hydrocupreene*, from hydroquinene or ethylhydrocupreene heated 7 hrs. at 145–50° with 5 parts HCl, dild., shaken with Et_2O, made alk. with NaOH, again shaken with Et_2O, extd. from soda soln. with much Et_2O, dried, treated with charcoal, evapd., taken up in dil. acid, neutralized, fractionally extd. with Et_2O with occasional additions of soda (the first exts. removing resins), washed with soda, evapd., taken up in Me_2CO, treated with H_2O to permanent turbidity and allowed to stand, stout quadrangular columns with 2 H_2O from dil. Me_2CO, m. 85–6° and (anhydrous) sinters about 65°, m. 155°; its solns. easily assume a reddish shade; it does not fluoresce in acids, immediately reduces $KMnO_4$ in H_2SO_4, gives only a faint green reaction with Br water-NH_4OH, together with a green fluorescence, gives a brown-red color in concd. alc. soln. with

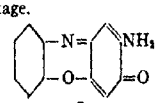
$FeCl_3$, dissolves in concd. H_2SO_4 without color but with green-blue fluorescence, $[\alpha]_D^{20}$ 27.1° (alc., *c* 1.4006); stratified in NaOH with dil. Br water it forms an olive-green ring and on shaking and adding more Br yields a faintly yellow-green soln. with faint green fluorescence. *Dihydrochloride*, yellow quadrangular columns with 3 H_2O from HCl (d. 1.06), anhydrous crystals from MeOH-AcOEt, m. 167°. Desoxyquinine, from quinine chloride and Fe wire in H_2SO_4, long flat needles with 2 H_2O from Me_2CO-H_2O, m. 51–2°, shows blue fluorescence in HNO_3 and a positive thalleioquin reaction, immediately decolorizes $KMnO_4$, dissolves in H_2SO_4 (d. 1.84) without color but with strong blue fluorescence, $[\alpha]_D^{20}$ (hydrated) 89.4°, (anhydrous) −99.9°, −99.6° (alc., *c* 1.8064, 0.9128, 1.6175, resp.). *Dihydrochloride*, yellowish needles, m. about 130°. *Desoxyethylcupreine*, viscous yellowish oil obtained in cryst. form only once, $[\alpha]_D^{20}$ −98.5° (alc., *c* 1.4816), forms with HCl (d. 1.06) a difficultly sol. *dihydrochloride*. *Desoxycupreine*, obtained only as a varnish from desoxyquinine or desoxyethylcupreine with HCl (d. 1.125) at 145°. Desoxyhydroquinine, from hydroquinine chloride, long flat needles with 3 H_2O from 50% Me_2CO, contracts 61°, m. turbid 68–9°, largely solidifies and m. again 95°, is relatively stable towards $KMnO_4$, $[\alpha]_D^{20}$ (hydrated) −80.15° (alc., *c* 2.2896); *dihydrochloride*, long quadrangular needles. *Desoxyethylhydrocupreine*, from ethylhydrocupreine chloride with Fe filings in H_2SO_4 or from desoxyethylcupreine with Pd and H, thick yellowish oil insol. in H_2O and alkalies, shows blue fluorescence in acids, is stable for some time towards $KMnO_4$, gives a green color with Br water-NH_4OH, $[\alpha]_D^{20}$ −85.6° (alc., *c* 1.6952). Desoxyhydrocupreine, from desoxyhydroquinine or desoxyethylhydrocupreine heated 8 hrs. at 145° with 5 parts HCl (d. 1.125), flat table-like needles from $CHCl_3$-Et_2O, 4- or 6-cornered columns from dil. Me_2CO, m. 182°, dissolves turbid in concd. NaOH, gives a red color with $FeCl_3$ in concd. alc. soln., does not fluoresce in HNO_3, instantly reduces $KMnO_4$ in H_2SO_4, gives only a faint green-yellow color with Br water-NH_4OH but at the same time a strong green fluorescence changing to pure blue on addition of alc., shows blue fluorescence in H_2SO_4 (d. 1.84), $[\alpha]_D^{20}$ −79.1°, −80.2° (alc., *c* 1.2324, 1.7200), gives when stratified in NaOH with dil. Br water a bluish green ring forming on shaking and adding more Br a colorless soln. with blue fluorescence. *Dihydrochloride*, fine microneedles from EtOH-AcOEt, sinters 90°, m. 112°. Desoxyquinidine, seps. from aq. Me_2CO with 2 H_2O, m. 82°, $[\alpha]_D^{20}$ (hydrated) 174.4° (alc., *c* 1.7684). Hydroquinidine, from quinidine by catalytic reduction, prismatic columns losing 4.41–5.23% in wt. over H_2SO_4 and m. 167–8°, $[\alpha]_D^{20}$ 231.3°, 230.4° (alc., *c* 2.9216, 2.6304), 233.6° (1 vol. 96% alc. + 2 vols. $CHCl_3$, *c* 2.3544), yields two forms of the basic sulfate; above 20°, needles with 3 H_2O; below 10°, stout hexangular table-like prisms with 18 H_2O. Hydroquinidine chloride was obtained only as a brownish resin; with Fe wire in H_2SO_4 it gave desoxyhydroquinidine, stout columns with 2 H_2O from 50% Me_2CO, m. turbid 72–3°, clear 95–7°, gives a positive thalleioquin test, shows blue fluorescence in HNO_3 and H_2SO_4, is relatively unstable towards $KMnO_4$-H_2SO_4, $[\alpha]_D^{20}$ (hydrated) 133.6° (alc., *c* 2.0064). *Desoxyhydrocupreidine*, from desoxyhydroquinidine heated 7 hrs. at 145° with 5 parts HCl (d. 1.125), stout tablets with 2 H_2O from moist Et_2O, sinters above 80°, m. turbid 96–7°, clear 160°, stout pointed needles from dil. Me_2CO, m. 96–7°, warts of flat needles from $CHCl_3$-Et_2O, m. 176–7°, sol. in H_2SO_4 (d. 1.84) with blue fluorescence, $[\alpha]_D^{20}$ 151.0° (alc., *c* 1.0193), gives in NaOH with dil. Br water an olive-greenish gray ring changing on shaking and adding more Br to a greenish yellow soln. with relatively strong blue fluorescence. C. A. R.

Oxidation of *m*-substituted *o*-aminophenols. K. v. Auwers, E. Borsche and R. Weller. Marburg. *Ber.* **54B**, 1291-316(1921); cf. *C. A.* **10**, 200.—A continuation of the investigation of the yellow substance formed by the oxidation with atm. air of 3,5,2-$Me_2(H_2N)C_6H_2OH$ (A) has shown that it is *3,5-dimethyl-2-amino-1,4-benzoquinone-*

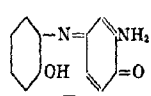
4-[dimethyl-6-hydroxyphenyl] imide, $O:C_6HMe_2(NH_2):NC_6H_2Me_2OH$ (B). B is best prepd. by shaking 70 g. A in 800 cc. of 4% NaOH 24 hrs. in a large flask connected with an O gasometer (yield, 50 g.); if the soln. is heated to boiling before shaking with the O and during the oxidation is again warmed occasionally, the reaction proceeds with considerably greater rapidity and in small-scale expts. the yields under the latter conditions are even better; with H_2O_2 under the most varied conditions as the oxidizing agent the yield of oxidation product is only about 0.5 of the A used. B seps. from C_6H_6 in stout orange-yellow crystals, m. 185°, mol. wt. in freezing C_6H_6 273, in $C_{10}H_8$ 272–3. If 1 g. B is stirred with 5 cc. 2 *N* HCl there is formed an oily or almost clear soln. which, however, at once begins to solidify to a thick magma of brick-red felted needles of the *hydrochloride*, partially sol. in pure H_2O, most of it being hydrolyzed and remaining behind as the yellow B; if an HCl soln. is evapd. *in vacuo* the salt remains as a brick-red cryst. mass but if it is evapd. on the H_2O bath the product is yellow-brown, only partially sol. in H_2O and converted by it into the free B; finally, dry HCl passed into B in C_6H_6 gives the salt in red crystals. *Chloroplatinate*, finely granular, dark orange ppt. *"Oxime"* or *3,5-dimethyl-2-amino-4-[2,4-dimethyl-6-hydroxyanilino]phenylhydroxylamine*, from 1 g. B boiled 12 min. with 0.78 g. $NH_2OH.HCl$ in alc., allowed to stand a long time and pptd. with dil. NH_4OH, light brownish yellow leaflets from MeOH-H_2O (3:2), m. 199–200°, sol. in alkalies and acids with yellow color. *"Phenylhyrazone"* or *3,5-dimethyl-2-amino-4-[2,4-dimethyl-6-hydroxyanilino]azobenzene*, from equimol. amts. of B and $PhNHNH_2$ in a little AcOH allowed to stand 2 days at room temp. and treated with H_2O, orange-red needles after repeated pptn. from MeOH with dil. HCl, m. 294–6°, difficultly sol. in dil. mineral acids, insol. in alkalies. *"Semicarbazone"* or *3,5-dimethyl-2-amino-4-[2,4-dimethyl-6-hydroxyanilino]benzeneazocarboxamide*, from B boiled with 2 mols. $H_2NCONHNH_2.HCl$ in dil. alc. and concd. after about 0.5 hr., the resulting *hydrochloride*, m. 267°, being decompd. in hot H_2O with excess of NH_4OH, fine yellow needles from MeOH, m. 206–7°, sol. in acids and alkalies with yellow color. If B is allowed to stand 1 day at room temp. with Ac_2O or heated on the H_2O bath with 5 parts of the Ac_2O until a sample on rubbing with soda gives a product no longer sol. in dil. HCl or the mixt. is boiled 4–5 min., then added to an excess of soda, rubbed until the Ac_2O is decompd. and the ppt. has become granular, freed from any unchanged B with cold dil. HCl and from the di-Ac deriv. with a little boiling MeOH, there is obtained a *monoacetyl derivative*, also obtained from B dissolved in just the necessary amt. of C_5H_5N on the H_2O bath, cooled with ice, slowly treated with 2 mols. AcCl, allowed to stand 24 hrs., filtered and rubbed with 5% H_2SO_4, orange-yellow leaflets from AcOH containing some H_2O, m. 219°. If, on the other hand, the B is heated 24 hrs. on the H_2O bath with 5 parts Ac_2O, poured into H_2O, digested with soda and then with dil. HCl, it gives the *O,N-diacetyl derivative*, short flat S-yellow needles from MeOH or dil. AcOH, m. 149°. *N-Propionyl derivative*, from 2 g. B and 2 g. EtCOCl in C_5H_5N, fine flat yellow needles from AcOH, m. 182–3°. The mono-Ac deriv. heated on the H_2O bath with 20 parts $(EtCO)_2O$ until dissolved (about 24 hrs.) gave an *O-propionyl-N-acetyl derivative*, yellow needles from AcOH, m. 139–40°. When 5 g. B is rubbed with 15 cc. concd. HCl and 100 cc. H_2O, dild. with 500 cc. H_2O, warmed to 60–70°, treated dropwise with concd. HCl until the soln. is clear, cooled with ice and treated, with vigorous turbining, with 1.2 g. $NaNO_2$ in 5 cc. H_2O, there seps. a foamy mass of a reddish yellow substance, flat red-yellow needles from AcOH, deflagrate 175°, with 15.3% N, which are possibly the free *diazonium base*, $C_{16}H_{17}O_3N_3$; if, after diazotizing as above, the soln. and ppt. are allowed to stand 3 days on the H_2O bath, there is obtained the expected *phenol* $C_{16}H_{17}O_2N$, which seps. in yellow-red amorphous flocks, m. 140–60°, when its soln. in 1% NaOH is filtered into excess of dil. HCl. When 2 g. B is heated 12 hrs. at 120–30° with 5 cc. concd. HCl and 5 cc. AcOH the chief product is A, identified

by its conversion in alk. soln. with air into **B**; there is also formed a dark amorphous substance insol. in H_2O from which no definite product could be obtained. That the other cleavage product which might be expected to result from **B**, *viz.*, anaminoxyloquin, one could not be isolated is not surprizing, as such a compd. would certainly tend to yield under the conditions of the expt. complicated condensation products, which probably were contained in the dark resin. Hoping a *N*-dimethylaminoquinone would be more stable, an attempt was made to prep. the *N*-Me_2 deriv. of **B**; 5 g. **A**.HCl was heated 7 hrs. at 170-80° with 15 g. MeOH, made alk., distd. with steam, taken up in Et_2O and dried with Na_2SO_4, giving *o-dimethylamino-sym-m-xylenol*, b_{18} 154–6°, $d_4^{20.5}$ 0.9955, *n* 1.51811, 1.52225, 1.53437, 1.54476 for α, D, β and γ at 20.6°, $E\Sigma$ 0.22, 0.22, 16%, 20% for α, D, $\beta - \alpha$ and $\gamma - \alpha$, resp.; *phenylurethan*, from 0.7 g. of the phenol and 1 g. PhNCO heated on the H_2O bath with 0.05 g. Na in 7 cc. dry Et_2O, fine felted needles from heavy benzine, m. 132–3°. When, however, **B**.HCl was similarly heated with MeOH, the products were chiefly **A** and a small amt. of the above di-Me deriv. *o-Amino-p-bromo-sym-m-xylenol* (**C**), from **A**. HCl rubbed with CS_2, treated with an equiv. of Br in CS_2, evapd., taken up in dil. NaOH, filtered and pptd. with AcOH, scales with fatty luster from C_6H_6, m. 136–8°, also obtained by heating for a few min. with 20 parts HCl (1:1) *o-aceto-p-bromo-sym-m-xylenol oxime*, fine needles from C_6H_6, m. 188°, which is prepd. from $Me_2(HON:CMe)C_6H_2OH$ and 2 mols. Br in CS_2. *o-Nitro-p-bromo-sym-m-xylenol*, obtained in 90% yield from $BrMe_2C_6H_2OH$ in 5 parts AcOH at 25–30° slowly treated with an equimol. amt. of concd. HNO_3 and heated a short time on the H_2O bath, also by dropping the $BrMe_2C_6H_2OH$ in AcOH into a mixt. of 1 part concd. HNO_3 and 2 parts AcOH, dilg. with H_2O and distg. with steam, needles from petr. ether, become colored in the light, m. 140–40.5°, gives with 2 *N* NaOH a yellow *sodium salt* sol. on diln. with deep yellow color: **C**.HCl (8.3 g.) in 50 cc. H_2O and 20 cc. alc. diazotized with 7–8 cc. concd. HCl and 2.1 g. $NaNO_2$ in 15 cc. H_2O, then poured into 12 g. NaOH in 36 cc. H_2O and treated with the Na_2SnO_2 soln. from 9.5 g. $SnCl_2$ acidified and distd. with steam, gives pure 4,3,5-$BrMe_2C_6H_2OH$, m. 116°, while 5 g. **A**.HCl diazotized in 5 cc. concd. HCl and 30 cc. H_2O with 2.2 g. $NaNO_2$ in 15 cc. H_2O, then poured in the course of 10 min. into a boiling soln. of 4.6 g. $CuSO_4$, 13 g. KBr, 3.5 g. concd. H_2SO_4, 6 g. Cu and 35 cc. H_2O, heated 15 min. longer on the H_2O bath and distd. with steam gives the isomeric *o-bromo-sym-m-xylenol*, yellow oil with a strong phenol odor, b_{18} 126°, seps. from low boiling petr. ether in stout flat prisms, m. 54°. **C** (1 g.) in 14 cc. of 2 *N* NaOH and 20 cc. H_2O shaken 1.5 hrs. with O yields *3,5-dimethyl-2-amino-1,4-benzoquinone-4-[2,4-dimethyl-3-bromo-6-hydroxyphenyl]imide*, brown-red in tables with blue surface luster from MeOH, m. 199–200°, also obtained from 1 g. **B** 15–20 cc. cold AcOH treated dropwise with 1.2 g. Br in 10 cc. AcOH and after some hrs. heated for a short time on the H_2O bath. 3,5-$MeBrC_6H_2OH$ was prepd. by Neville and Winther's method from 2,5-$H_2N(O_2N)C_6H_2Me$ but the details of each successive step had to be worked out, as but few exact directions are given in the literature (cf. Weller, *Diss. Marburg* 1920); the 3,5-$Br(H_2N)C_6H_2Me$ b_{15} 150–1°, the $Br(HO)C_6H_2Me$ b_{28} 161–2°. *m-Bromo-m-cresyl methyl ether*, from 59 g. of the cresol in 520 cc. of 4% NaOH shaken with 37 g. Me_2SO_4 (yield, 35 g.), refractive oil, b_{20} 139–40°. *p-Benzeneazo-m-bromo-m-cresol*, from 2 g. of the cresol in 200 cc. of 1% NaOH treated, with turbining, with an equiv. amt. of PhN_2Cl, filtered from the bisazo compd. (below) and acidified with AcOH, ruby-red leaflets from benzene, m. 97–9°; *bisbenzeneazo-m-bromo-m-cresol*, brick-red prisms from AcOH, m. 171–3°. *o-Aceto-m-bromo-m-cresol*, from 35 g. of the $MeBrC_6H_2OMe$ and 14.2 g. AcCl in 3 vols. CS_2 slowly treated with 27 g. $AlCl_3$, allowed to stand overnight, boiled till the evolution of HCl ceased, again treated with 14.2 g. $AlCl_3$ and boiled, freed from the CS_2 by distn., decompd. with ice and HCl, taken up in Et_2O, exhaustively extd. with 8% NaOH, acidified and distd.

with steam, stout prisms from light benzene, m. 50–2°; *semicarbazone*, needles from alc., m. 218–20°; *oxime* (13 g. from 15 g. of the ketone and 15 g. $NH_2OH.HCl$ in 225 cc. of 8% NaOH allowed to stand 3 days at room temp.), felted needles from C_6H_6, m. 127°; boiled with 20 parts HCl (1:1) and evapd. to incipient crystn. as soon as the soln. becomes darker and treated with Na_2SO_3 it gives *o-amino-m-bromo-m-cresol* (yield, 70%), stout needles from H_2O containing SO_2, m. 140–1°; *hydrochloride*, pearly leaflets, m. 225–8°. The cresol (1.5 g.) in 20 cc. alc. and 20 cc. AcOH treated, first hot, then at room temp., in the course of 12 hrs. with 500 g. of 2% Na-Hg with occasional additions of H_2O to dissolve the NaOAc crystg. out and of AcOH to keep the soln. always acid, then acidified with H_2SO_4, filtered, concd. to renewed crystn., treated with excess of NaOH and shaken with BzCl gives a product which after 2 crystns. from MeOH m. 143–4° and when mixed with a sample (m. 152°) of 5,2-Me(BzNH)C_6H_3OBz (see below) m. 147–8°. *3-Bromo-5-methyl-2-amino-1,4-benzoquinone-4-[2-bromo-4-methyl-6-hydroxyphenyl]imide*, from 1 g. of the cresol in much H_2O and 3 drops of 8% NaOH treated 24 hrs. at room temp. with a vigorous current of air, dark yellow leaflets from C_6H_6, brownish red tablets from alc., m. 218–9°, easily sol. in dil. acids, repptd. by alkalies. *o-Amino-m-cresol*, from 40 g. 5,2-Me(O_2N)C_6H_3OH boiled with 50 g. Sn and 250 cc. concd. HCl until a test dild. with H_2O remains clear, then dild. with about 2 l. H_2O, freed from Sn on the H_2O bath with H_2S, concd. in a current of H_2S to a small vol., nearly neutralized with NaOH and pptd. with concd. Na_2SO_3, felted needles from aq. SO_2 or C_6H_6, soon turns brown in the air, m. 157–9°; *dibenzoyl derivative*, m. 152° after 4, 162–3° after 6 crystns. from MeOH. *5-Methyl-2-amino-1,4-benzoquinone-4-[4-methyl-6-hydroxyphenyl]imide* (9 g. from 17 g. of the cresol in 2.5 l. H_2O and a few drops concd. $(NH_4)_2CO_3$ treated 48 hrs. with a current of air), brick-red crystals from C_6H_6, m. 185–6° after repeated crystns. (Kehrmann and Bühler, *Ber.* **39**, 137(1906), give 176–7°); 2 g. heated 12 hrs. at 120–30° with 5 cc. concd. HCl and 5 cc. AcOH yields a small amt. of the original cresol; *N-acetyl derivative*, from 1 g. of the imide in just the necessary amt. of C_5H_5N treated dropwise with 1.2 g. AcCl, allowed to stand 3 hrs. at 0°, filtered and poured into 300 cc. H_2O, brownish yellow leaflets from dil. AcOH or dil. MeOH, m. 177–8°. *"Semicarbazone"* or *5-methyl-2-amino-4-[4-methyl-6-hydroxyanilino]benzeneazocarboxamide*, golden yellow needles from alc., m. 195° (decompn.), obtained as the *hydrochloride* from 1.5 g. of the imide and 1.3 g. $H_2NCONHNH_2.HCl$ boiled 15 min. in aq. alc. under a reflux. Both forms (brick-red and yellow-brown) of the HCl salt of B dissolve in a little H_2O with the color of a $K_2Cr_2O_7$ soln. and both are electrolytes as shown by the Lodge-Nernst method; when a 0.01 *M* soln. of B in 0.01 *N* HCl containing 50% glycerol by vol. is placed in a U-tube and covered with 0.01 *N* HCl and an e. m. f. of 130 v. is applied to the system there is a distinct migration to the cathode of approx. the same rapidity for both forms of the salt; the ionic migration velocity is about 25 at room temp. B is of general interest in that, owing to the particular structure of the starting material, A, the condensation process between several mols. of a monomeric quinoneimide is stopped at the first stage. From the simplest *o*-aminophenol Fischer and Jonas (*Ber.* **27**, 2782(1894)) obtained by cautious oxidation a substance which they consider to be an aminophenoxazone (I). The present work makes it practically certain that the first product is II, thus tending to confirm F. and J.'s formula for the final product. In the oxidation of A the *m*-Me group hinders the further removal of H with consequent closure of the ring and formation of the tricyclic compd. and the condensation stops at the first stage.



I



II

C. A. R.

The occurrence of methyl *l*-inositol in an Australian poisonous plant (PETRIE) **11D.** Formation of hexachlorobenzene in the electrolytic preparation of chlorine (BOURION, COURTOIS) **4.** Photochemical apparatus (U. S. pat. 1,382,252) **1.**

Acetic acid. R. L. ANDREAU. U. S. 1,381,782, June 14. An acetate such as NaOAc is suspended in a paraffin oil, and H_2SO_4 is added to the mixt. to form HOAc which is immediately distd. The use of the oil serves to control the reaction and limit it to a simple double decompn.

Formaldehyde. G. C. BAILEY and A. E. CRAVER. U. S. 1,383,059, June 28. CH_2O is produced by passing MeOH vapor together with air in contact with V oxide at a temp. of 225–400°.

Phthaleins. A. L. RISPLER. U. S. 1,381,503, June 14. Phthalic anhydride is condensed with PhOH or other phenol in the presence of an anhydrous aromatic sulfonic acid which acts as a condensing and dehydrating agent for the production of phenolphthalein. $ZnCl_2$ may be used as an auxiliary condensing agent.

Sodium naphtholate. L. F. CHEBOTAREF. U. S. 1,381,280, June 14. Na naphthalene-β-sulfonate 15 is fused with NaOH 11 parts at a temp. of 280-350° and the upper layer formed on prolonged heating is removed and allowed to solidify. It is a basic Na naphtholate, $C_{10}H_7ONa + NaOH$.

11—BIOLOGICAL CHEMISTRY

HATTIE L. HEFT, EDGAR G. MILLER AND WILLIAM J. GIES

A—GENERAL

FRANK P. UNDERHILL

Bodily symptoms caused by emotion. F. H. KOOY. *Nederl. Maandschr. Geneesk.* **1,** 29–44(1920); *Endocrinology* **4,** 442.—Cannon has reported that emotion (fear, rage) causes hyperactivity of the sympathicus and a hypersecretion of adrenaline. K. found, in agitated patients with psychoses, a higher amt. of blood sugar and a higher blood pressure than normal. It is suggested that the changes in temp. (hysterical fever) and in the function of the intestines during emotion may perhaps be explained in the same way. H. G.

The cycle of cellular life. Physiological researches on the division of the cell. (Preliminary note.) M. HERLANT. *Ann. bull soc. roy. sci. med. nat. Bruxelles* **4,** 112–17(1920); *Botan. Abstracts* **7,** 107.—H. has sought to det. whether the permeability of the cortical layer of the protoplasm is const. during the entire duration of the cellular cycle. He has observed that the plasma membrane of the egg of the sea urchin is, according to the stage of the cell life, sometimes permeable and sometimes impermeable to salts. The lipoid state (semipermeable) and the albuminoid state (permeable) of the plasma membrane do not co-exist, but succeed each other periodically in the course of the cellular life. The physico-chem. equil. of the protoplasm, and not alone that of the cortical layer, depends in part on factors destroyed by the insol. substances in the lipoids (permeable phase) and in part on factors destroyed by the solvents of the lipoids (semipermeable phase). These phenomena are in accordance with the emulsion theory of protoplasm. H. G.

The oxygen dissociation of hemoglobin and the effect of electrolytes upon it. E. F. ADOLPH AND RONALD M. FERRY. Harvard Univ. *J. Biol. Chem.* **47,** 547–55 (1921).—Freshly defibrinated beef blood was centrifuged; the cells were washed 3 times with 0.9% NaCl and then dialyzed in 100-cc. collodion sacs for 48 hrs. against running H_2O and then against distd. H_2O in a refrigerator. In order to remove cations, the liquid

in the sacs was then either satd. with CO_2 and then dialyzed or was dialyzed against H_2O satd. with CO_2 and then against H_2O. The conductivity of the solns. containing approx. 14% hemoglobin was only rarely greater than 3×10^{-4} reciprocal ohms and that of one prepn. was 8×10^{-5} reciprocal ohms. When equilibrated against an air-H_2 mixt. of about 30 mm. O_2 tension, it was found that the addition of acids decreased the % O_2 satn., that of NaOH or of Na_2HPO_4 increased it, that of KCl or of NaCl or of a mixt. decreased it and that of urea or of sucrose left it unaffected. I. GREENWALD

Lipase studies. I. The hydrolysis of the esters of some dicarboxylic acids by the lipase of the liver. ADAM A. CHRISTMAN AND HOWARD B. LEWIS. Univ. Illinois. *J. Biol. Chem.* **47**, 495–505(1921).—"On the basis of the acidity developed when the lipase of hog liver was allowed to act upon the di-Et esters of succinic and malonic acids, it is considered that the reaction proceeded to an equilibrium which corresponded to the removal of one Et group from the di-Et esters. A substance was obtained from the products of the reaction between di-Et malonate and lipase which gave on analysis figures which were in good agreement with these required for mono-Et malonate. Lipase of hog liver was not able to effect the cleavage of mono-Et malonate or of K Et malonate. PrOEt was hydrolyzed by lipase in the presence of K Et malonate but not in the presence of H Et malonate." I. GREENWALD

The stability of tryptophan in baryta hydrolysis. HERBERT ONSLOW. *Biochem. J.* **15**, 383–91(1921).—When caseinogen is hydrolyzed by NaOH tryptophan is more rapidly destroyed than when $Ba(OH)_2$ is used. The destruction of tryptophan may be largely prevented by the addition of cryst. amino acids. BENJAMIN HARROW

The nature of the substances precipitated by mercuric sulfate from hydrolyzed caseinogen, with reference to the estimation and isolation of tryptophan. HERBERT ONSLOW. *Biochem. J.* **15**, 392–99(1921); cf. preceding abstr.—The $HgSO_4$ compd. pptd. from hydrolyzed caseinogen was found to contain leucine, cystine, tyrosine, glutamic and aspartic acids, histidine and proline. Lysine and arginine were absent. Combined tyrosine was found after severe acid hydrolysis; this indicates that this amino acid does not sep. quantitatively as early in digestion as was believed. A method is given for prepg. tryptophan, based on pptn. with $HgSO_4$, removal of Hg with H_2S, digestion a 2nd time with trypsin, and extn. with butyl alc. BENJAMIN HARROW

Studies of autolysis. VII. Autolysis of brain. CHARLES A. GIBSON, FREDA UMBREIT AND H. C. BRADLEY. Univ. Wisc. *J. Biol. Chem.* **47**, 333–9(1921); cf. *C. A.* **15**, 1143.—"Brain tissue autolyzes in the same way as other tissues thus far examd. though quant. on a smaller scale comparable to the low protein content of brain tissue. The speed and extent of the proteolysis is detd. by the H-ion concn. of the mixt. In alk. or neutral media autolysis is inhibited. It is increased in proportion to the acid added. The optimum acidity for autolysis of brain tissue is about 0.02 *N*, or much less than that for liver, kidney, and other epithelial tissues. The small amt. of acid required corresponds to the small amt. of protein present and made available for digestion by the addition of acid. Brain cells contain proteolytic enzymes which digest such added substrata as gelatin or peptone, as in other gland structures. The permanence of the protein structures of the brain appears to depend on the very perfect protection against asphyxia and CO_2 accumulation, which its large blood supply and its control of respiration insures. When asphyxia and acidosis do develop in brain tissue, it autolyzes like other tissues. The autolytic disintegration of the delicate protein structures of brain tissue appears to be an irreversible phenomenon, and is accompanied by loss of such characteristic functions as memory, habit, motor control, and consciousness." A. P. LOTHROP

Studies in wood decay. II. Enzyme action in Polyporus volvatus Peck and Fomes igniarius (L) Gillet. HENRY SCHMITZ. Univ. Idaho. *J. Gen. Physiol.* **3**,

795–800(1921); cf. *C. A.* **14**, 1561.—*Polyporus* gave positive tests for the following enzymes: esterase, maltase, lactase, sucrase, raffinase, diastase, inulase, cellulase, hemicellulase, glucosidase, rennet, and catalase. *Fomes*, in addition to the above-mentioned enzymes, showed the presence of urease. Evidence is presented which indicates that *Polyporus* is parasitic. CHAS. H. RICHARDSON

Studies on the regulation of osmotic pressure. I. The effect of increasing concentrations of gelatin on the conductivity of a sodium chloride solution. WALTER W. PALMER, DANA W. ATCHLEY AND ROBERT F. LOEB. Johns Hopkins Univ. *J. Gen. Physiol.* **3**, 801–6(1921).—The following conclusions are stated: "In pure gelatin solns. the cond. of the soln. increases with increasing concns., regardless of the H-ion concn. The actual value of the sp. cond. is greater at that reaction where the degree of ionization is greater. The addition of gelatin in increasing concns. to a 0.6% NaCl soln. affects the cond. in two ways: (*a*) At p_H 3.3 (where gelatin is highly ionized) the cond. increases with each added increment of gelatin. (*b*) At p_H 5.1 and 7.4 (where gelatin is less highly ionized) the cond. decreases with each added increment of gelatin." It is pointed out that at the reaction of the blood, the protein is so little ionized that the cond. decreases with each addition of protein owing to mechanical interference. A similar study is being made of cryst. egg albumin. CHAS. H. RICHARDSON

Actions between enzymes. H. VAN LAER. *Bull. soc. chim. Belg.* **28**, 340–6 (1919).—The maceration juice, sepd. at the moment of autolysis from a mixt. of dried yeast and water, contains an invertase, which is sensitive to both active and passive papaïn and to amylase. This sensitiveness is not shown by the juice sepd. after autolysis or by the limpid exts. from yeast killed by acetone. The liquids, obtained by macerating yeast killed by acetone with active solns. of papaïn or amylase, show a notable increase in inverting power, which is apparently due to the difference between the increase resulting from the liberation of invertase masked by the protoplasmic substances, and the diminution caused by a greater sensitiveness of the freshly liberated enzyme to the products of digestion of its cellular substrate. J. S. C. I.

Ice crystals which form on bare soils and on the stems of plants (BIRCKNER) **2**. The role of acetaldehyde in alcoholic fermentation (FERNBACH) (SCHOEN) **16**. Acidity of the hydrogen atoms of uric acid (BILTZ, HERRMANN) **10**.

B—METHODS AND APPARATUS

STANLEY R. BENEDICT

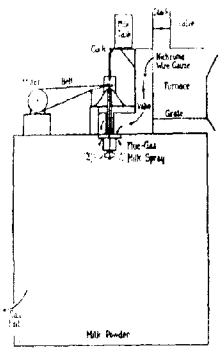
Simplified photomicrography. B. ROSSMANN. *Pharm. Ztg.* **66**, 587–8(1921).—A description with cut of an easily improvized app. for photographing animal and vegetable prepns. and parts, as also pharmacol. prepns., like calomel suspensions in vaseline. W. O. E.

An improved colorimeter for color inheritance study. HERBERT F. ROBERTS. *Plant World* **22**, 262–9(1919); *Botan. Abstracts* **6**, 291.—Improvements of the tintometer are described and illustrated. The instrument is said to be especially valuable in quant. measurement of color value in flowers, in a study of color inheritance, as in detg. the color value of segregates, and in quant. color detns. generally. H. G.

Note on a source of error in the colorimeteric methods for the estimation of cholesterol in tissue fats. J. A. GARDNER. *Biochem. J.* **15**, 376–78(1921).—It seems that alc. or some impurities in it (aldehydes?) give a color reaction with $CHCl_3$ and acetic anhydride. This is of importance, since in the estn. of the sterols of tissues the fats are hydrolyzed by boiling with alc. potash or sodium ethoxide. BENJAMIN HARROW

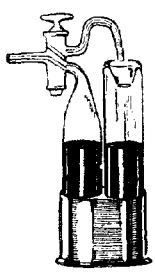
Methods of extracting and concentrating vitamines A, B, and C, together with an apparatus for reducing milk, fruit juices, and other fluids to a powder without destruction of vitamines. J. F. MCCLENDON. Univ. Minn. Med. School. *J. Biol.*

Chem. **47**, 411–20(1921).—"As the population increases, the question of food supply becomes more urgent, and the vitamines being necessary food constituents need to be conserved. It is therefore important to develop methods for extg. them from plants that are not considered edible and for preserving them in foodstuffs that require storage. Methods have been especially devized for vitamines A, B, and C. Each product is, in reality, a mixt. of vitamines with one predominating. By these methods the vitamines are extd. with very little loss, and concd. without the use of very expensive reagents. The unique features of the methods are believed to be: 1st, the extn. of vitamine A from green leaves or fruit skins by the use of high pressure (after moistening with alc.); 2nd, the sepn. of the resinous and lipoid material from the H_2O-sol. portion in extg. vitamine B by increasing the H-ion concn. up to the isoelec. point of these colloids; and 3rd, the removal of the sugars from the B and C exts. by fermentation with bakers' yeast. All processes are carried out in the absence of O, and the drying is done very quickly." H_2O-sol. B can be conveniently prepd. from wheat germ or yeast and H_2O-sol. C from fruits or tomatoes. The original must be consulted for the description of the details of the construction and operation of the drying app.



A. P. Lothrop

Apparatus used in determining the respiratory exchange in man. I. An adaptation of the French gas mask for use in respiratory work. Cameron V. Bailey. Post-Graduate Med. School and Hosp., N. Y. *J. Biol. Chem.* **47**, 277–9(1921).—The French gas mask is especially suitable for use in respiratory work as it covers the whole face and presents broad surfaces which closely engage the forehead, sides of the face and jaw; it is preferable to the half mask which must frequently be applied so firmly to avoid leaks that it causes extreme discomfort. **II. A sampling bottle for gas analysis.** *Ibid* 281–3. The bottle has a capacity of 60 cc. and contains gas enough for 6 detns. when used with the Henderson modification of the Haldane gas analyzer. There is no danger of diln. or loss of Hg.



A. P. L.

The determination of cresol by the phenol reagent of Folin and Denis. Robert M. Chapin. U. S. Dept. Agr., Bur. Animal Ind. *J. Biol. Chem.* **47**, 309–14(1921).—"The quality and intensity of color developed by a phenol with the reagent of Folin and Denis is dependent both upon the nature of the phenol and the compn. of the medium. The conditions affording colors of max. intensity and most consistently comparable when developed from differing phenols have been detd. Accurate quant. comparison between different phenols demands an empirical factor. By use of prescribed empirical factors and adherence to standard working conditions, the cresols may be detd. with fair accuracy as 'total cresol.'" Transfer to a 100-cc. volumetric flask such an amt. of the soln. to be analyzed as will yield a color closely approximating that given by 0.5 mg. of phenol which constitutes the standard. Add 3 cc. of the phenol reagent prepd. according to the formula of Wu (*C. A.* **14**, 2895). Dil. to 63 cc., add 5 g. of pure powd. $NaHCO_3$, and swirl the flask until soln. is complete (2 min.). Allow to stand for ½ hr. to insure complete inactivation of excess reagent. Add 5 cc. of a 10% soln. of anhydrous Na_2SO_3, make up to vol., mix, and filter, the first 25 cc. of filtrate being discarded. Compare immediately in a colorimeter, the standard being set at 20 mm. Wt. of cresol/wt.

of phenol gives a ratio, for *o*-cresol, of 1.19; *m*-cresol 1.09; *p*-cresol 1.22; com. tricresol 1.16, taking it as a 35 : 40 : 25 mixt. of the isomers. If the compn. of the cresol be known to the extent that it is either predominately a certain one of the isomers or the ordinary com. mixt., the error need not be more than 5% if the proper factor is employed. The method can be practically applied for the *detn. of phenolic preservatives in serums*, etc., as follows: To 1 cc. of serum in a 300-cc. flask, add 125 cc. of H_2O, 4 cc. of 1:3 (by vol.) H_2SO_4, 4 cc. of a 12% soln. of silicotungstic acid, and a fragment or two of pumice. The silicotungstic acid is an efficient precipitant for the substances which cause foaming and should be procurable without difficulty as it is used extensively in the detn. of nicotine. Connect the flask with a nearly vertical condenser by a three-bend tube. Heat slowly to boiling and collect the distillate in a 200 cc. volumetric flask. Withdraw the flame when 100 cc. of distillate have been obtained. Add 100 cc. more H_2O to the distn. flask and continue the distn. until the receiving flask is filled nearly to the mark. Make up to vol. and mix. Transfer 20 or 50 cc., depending on whether phenol or cresol is the preservative probably present, to a 100-cc. volumetric flask and make the detn. as described above. If the readings on the colorimeter are too far from 20 mm., repeat the detn. on a more appropriate vol. of distillate. If it is necessary to distinguish further between phenol and cresol, use the method previously described by C. as a qual. test (*C. A.* **14**, 2772). Transfer 10 cc. of the distillate to a test-tube, and to a similar tube a colorimetrically equiv. amt. of the standard phenol dild. to 10 cc. To each tube add 5 cc. of the special Millon reagent and heat as described. The resulting colors will plainly indicate whether the preservative employed was essentially phenol or cresol. Cf. *C. A.* **14**, 3387. A. P. LOTHROP

Selection of analysts for color work in chemistry (O'BRIEN) 7.

C—BACTERIOLOGY

A. K. BALLS

Studies on the food relations of Fusarium lini. YOSHIHIKO TOCHINAI. *Ann. Phytopath. Soc. Japan* **1**, 22–33(1920); *Botan. Abstracts* **7**, 64.—The following substances were tested as sources of C: nine carbohydrates—*viz.*, glucose, levulose, galactose, sucrose, maltose, lactose, sol. starch, inulin, and arabin—in 2% solns.; six org. acids—*viz.*, malic, succinic, maleic, fumaric, racemic, and citric—in 1 and 0.1% solns.; and glycerol, mannitol, vanillin, thymol, and α-naphthol in 2% solutions. The chemicals were added in the above indicated quantities to a standard nutritive soln. prepd. as follows: NH_4NO_3, 1 g.; KH_2PO_4, 0.50 g.; $MgSO_4$, 0.25 g.; and redistilled water 1000 g. As sources of N, $(NH_4)_2SO_4$, $NaNO_3$, KNO_3, peptone, and urea in 2% solns., and acetamide, succinamide, dicyandiamide, and asparagine in 1% solns. were tested. Each chemical was added to a standard nutritive soln. of the following compn.: KH_2PO_4, 0.50 g.; $MgSO_4$, (crystal) 0.25 g.; cane sugar, 20 g.; and redistilled water, 1000 cc. Results were checked at the end of two weeks growth. The carbohydrates tested gave the following dry wts. in g. of mycelia: inulin 0.299; glucose 0.274; arabin 0.147; maltose 0.151; sol. starch 0.125; levulose 0.084; galactose 0.072; sucrose 0.044; and lactose 0.039. Org. acids as source of C were unfavorable to the fungus, which could develop only in low percentages, such as 0.1%. As indicated by the growth made, the org. acids may be arranged as follows in descending order: succinic, malic, citric, fumaric, maleic, and racemic. In the nutritive soln. contg. racemic acid the *d*-tartaric was more readily assimilated than the *l*-tartaric acid, as detd. by the change in optical activity. Mannitol was a favorable source of C, 0.24 g. (dry wt.) of mycelium being produced, while glycerol gave but 0.024 g. The phenol derivs. prevented growth. Org. N compds. are far better sources of N than inorg. compds., the dry wts. of mycelium in g. being as follows: peptone 0.448; urea 0.251; $NaNO_3$ 0.198; NH_4 phosphate 0.194; $(NH_4)_2SO_4$

0.038; and KNO_3 0.012. The amides are generally good sources of N for this fungus, the following dry wts. in g. of mycelia being obtained: asparagine 0.288; acetamide 0.173; dicyandiamide 0.516; and succinamide 0.143. H. G.

Determination of the hydrogen-ion concentration of culture media. A. PONSELLE. *Bull. inst. Pasteur* **18**, 601–10(1920); *Botan. Abstracts* **7**, 310.—This is a short review of the theory of acidity and of the principles underlying the methods for the detn. of H-ion concns. A few examples of simple calcns. to be used in detg. p_H values and a short exposition of the technic of the colorimetric methods are given. The work of Sörensen, Hörwitz, Meyer and Qstenberg, Clark and Lubs, Homer, Ponselle, Barnett and Chapman, and of Fennel and Fisher is reviewed. The reader is cautioned against the use of the colorimetric method in adjusting the reaction of deeply colored media, and reference is made in this connection to the electrometric methods. The contribution is in fact a guide to be used in daily bacteriol. operations and not a theoretical discussion of the subject. H. G.

Ectoenzymes of streptococci. M. S. TONGS. *J. Am. Med. Assoc.* **73**, 1277(1919); *Abstracts Bact.* **3**, 333–4.—A number of streptococci were tested for enzyme formation and ability to digest starch and casein. The media employed were agar with a suspension of starch and fat-free milk with agar. When digestion of starch or agar occurred a clear zone formed about the colonies. A small amt. of the clear area on the starch medium was removed and tested with Fehling soln. to show that maltose had been produced. By pouring Lugol soln. over the colonies a red colored zone outside of the clear zone indicated the presence of erythrodextrin. Casein digestion was indicated by the formation of a clear zone around the colonies which contained no protein precipitable with AcOH. Among hemolytic streptococci there seem to be 3 groups: one digesting casein, one starch, and the other neither casein nor starch. Among the green-producing streptococci only two groups are indicated: one digesting casein, and one without action on either starch or casein. H. G.

The lactic acid bacteria. S. ORLA-JENSEN. *Mem. acad. sci. let. Danemark (Sec. Sci.)* **VIII, 5**, 81–196(1919); *Botan. Abstracts* **6**, 25.—"The biochem. portion of this monograph represents a contribution of the highest value to our knowledge of the physiology of a puzzling bacterial complex. From a systematic standpoint it is less illuminating. The evidence for combining the streptococci and the Bulgarian bacillus group in one family is suggestive, but hardly conclusive; while as in previous communications the author appears entirely innocent of any knowledge of the principles of biological nomenclature or of any respect for the work of previous investigators. His genus *Betacoccus* is apparently *Leuconostoc* of VAN TIEGHEM, and his *Thermobacterium* is certainly *Lactobacillus* Beijerinck; while many of his specific names are merely confusing synonyms of perfectly valid names given by previous investigators." H. G.

Plant groups that fix free nitrogen. A. CAUDA. *Nuovo giorn. botan. ital.* **26**, 169–78 (1919); *Botan. Abstracts* **6**, 121; cf. *C. A.* **15**, 543.—*Bacillus cruciferae*, isolated from the roots of various cruciferous plants (*Raphanus, Sinapus, Brassica*), was found to fix free N, especially when cultivated on liquid media having an excess of Ca carbonate and a deficiency of N. The amt. of N fixed by the organism nearly equals that obtained from *Azotobacter* and surpasses *B. radicicola*. *B. cruciferae* forms round, whitish colonies of viscid consistency. Older colonies turn yellow, rose, or red brown. The organism is rod shaped and forms chains; it is stained yellow with KI and blue with Löffler's stain and methylene blue. H. G.

Comparative utilization of various constituents of the cell wall by Xylaria hypoxylon L. C. L. GATIN AND M. MOLLIARD. *Rev. gén. botan.* **32**, 216–25(1920); *Botan. Abstracts* **7**, 63.—A study of the digestive action of a wood-destroying fungus (*Xylaria hypoxylon*) on isolated constituents of the cell wall in aseptic cultures. The constituents

under investigation were added to a mineral nutrient soln. made up as follows: tap water, 100 cc.; KNO_3, 0.2 g.; NH_4 phosphate, 0.05 g.; $MgSO_4$, 0.05 g. Glucose and starch were also used for comparison. Of all the substances tried, pectin was the most readily utilized by *Xylaria*; 1.633 g. were used in building up 0.693 g. dry wt. of mycelium. Then followed in order xylose and glucose, mannogalactan of the carob, arabinose (about half as well used as pectin), starch, and xylan. Good growth was also obtained on corrozo and the mucilage of flax, whereas cherry gum was only slightly used, and gelose not at all. A further expt. showed lignin to be very readily utilized. H. G.

Enzyme formation by Penicillium glaucum. H. VON EULER. *Fermentforschung* **4**, 242–57(1920–21).—Expts. were made on the inversion of different sugar solns. by *P. glaucum*. The conditions of the expts. as to percentage of sugar, age, and state of fructification of the fungus, and temp. were varied. The saccharase content of the fungus as evidenced by the inversion produced was calcd. from the formula, inversion capacity = inversion const. × wt. of sugar/wt. of dry substance of fungus. It was found that the inversion capacity was highest on the fourth day of growth and at a temp. under 16°. The conidia of the fungus had only a third of the inversion capacity of the mycelium. The highest inversion capacity was exhibited in solns. of cane sugar and galactose. The general conclusion was that *P. glaucum* contains but a tenth of the saccharase content of bottom yeast and a sixth of that of top yeast. J. C. S.

Microchemistry of microörganisms. I. Biochemistry of Bacillus mesentericus vulgatus. W. GRIMMER AND B. WIEMANN. *Forsch. Geb. Milchwirt.* **1**, 2–18(1921).—*Bacillus mesentericus vulgatus* contains a proteolytic enzyme which in a very weak acid medium hydrolyzes casein to its simplest constituents. The following products were identified: alanine, valine, leucine, tyrosine, aspartic acid, glutamic acid, proline, arginine, lysine, histidine, tryptophan, and perhaps phenylalanine. In the presence of lactose, proteolysis is not so complete and the following products were identified: putrescine, cadaverine, tryptamine, tyrosol, and NH_3. J. C. S.

The role of potassium in the chemistry and reproduction of fungi. MARIN MOLLIARD. *Compt. rend.* **173**, 100–2(1921).—If instead of using a well balanced soln. for the culture of *Sterigmatocystis nigra*, one is used that is low in N, growth soon ceases, and reproduction occurs. In a soln. containing very little K growth soon ceases and the mycelium remains sterile. If the latter soln. is replaced after 10 days by one containing only sugar and KCl, conidiophores are formed; if by one containing only sugar the fungus remains sterile. Similar results were obtained on the effect of K on sexual reproduction in a species of *Eurotium*. T. G. PHILLIPS

Influence of peptone on indole formation by Bacillus coli. F. W. TILLEY. U. S. Bur. Animal Ind. *Am. J. Pub. Health* **11**, 834–6(1921).—T. concludes that the varying compn. of the different kinds of peptone available in this country may cause a typical strain of *B. coli* to give a negative, weak or strong reaction for indole, depending on the kind of peptone used and the time of incubation. It is advizable to test each new lot of peptone used in order to det. the suitability for indole production and also the optimum incubation time. A test for the presence of *tryptophan* will usually indicate the relative value of any given sample of peptone for use in making indole tests.

NATHAN VAN PATTEN

Action of microörganisms on crude petroleum (TAUSZ) **22**.

D—BOTANY

CARL L. ALSBERG

Culture tests with soy beans. Occurrence of urease in parts of the plant other than the seeds. D. H. WESTER. *Pharm. Weekblad* **58**, 113–9(1921).—The young plants contain urease in the root, stem, seed pods and leaves. A. W. Dox

The "brown rot" disease of fruit trees, with special references to two biologic forms of Monilia cinerea Bon. II. H. WORMALD. *Ann. Botany* **34**, 143–72(1920); *Botan. Abstracts* **6**, 188–9.—Continuing his work of comparing the organisms which bring about the different types of "brown rot" on fruits in England, W. detd. that the strain of *Monilia cinerea* infecting flowering shoots and cankers of apple trees (forma *mali*) differs from the organism isolated from plum (forma *pruni*) in its greater capacity to secrete an enzyme which oxidizes tannin. The oxidizing enzyme produced freely by *M. cinerea* forma *mali* was demonstrated by use of gum guaiac emulsion as well as by pyrogallic acid. The enzyme did not show any action upon tyrosine or hydroquinone but did produce a brownish yellow color in solns. of tannic, gallic and pyrogallic acids. It was produced by "forma *mali*" in liquid culture media, infected fruits and spurs of apple and its presence is correlated by W. with the greater virulence toward apple shown by this form over that shown by the form isolated from *Prunus*. The distinctions between *M. fructigena* and *M. cinerea* are summarized. Within the species *M. cinerea* at least two forms are recognizable culturally and parasitically distinct. H. G.

Physiology of anthocyan and chemistry of chlorophyll. J. COSTANTIN. *Ann. Sci. Nat. Bot.* X. **1**, xxxviii–lii(1919); *Botan. Abstracts* **7**, 62.—C. discusses the present status of the knowledge of anthocyan and chlorophyll. He refers to Combes' work in 1913 in which a treatment of a yellow flavone pigment derived from *Vitis* with nascent H gave a substance said to have been anthocyan. C. states that the reverse process of oxidation of anthocyan gave yellow flavone. The work of Willstätter confirmed Combes' conclusions. Such work linked up with the problems concerning glucosides and Combes' expts. with absorption of these in plants is referred to. C. calls attention to the belief of some that anthocyan results from an oxidation. This hypothesis is supported by the discovery that oxidase distribution parallels anthocyan distribution. Palladin made anthocyan one of his respiration pigments. Wheldale's attempt to explain anthocyan production in *Antirrhinum* on a genetic basis is "curieuse" to C. but he deems it preferable to Bateson's assumption of determinants. Nicolas in 1919 suggested a study of green and purple plants of the same species in an attempt to resolve contradictions in oxidation and reducing theories of anthocyan formation. Nicolas found greater acidity in the red-leaved varieties and the formation of these org. acids locked up some O, reducing therefore the respiratory quotient. The using up of O, therefore, is not directly a result of anthocyan production. Chlorophyll is thought now to have the formula: $(C_{20}H_{39}OOC)$ $[C_{31}H_{29}N_4Mg]$ $(COOH)$ $(COOCH_3)$. Treatment with alc. will produce a substitution of C_2H_5 for the phytol group $C_{20}H_{39}$ and give Willstätters' crystallizable chlorophyll. H. G.

Flora of the Sardinian waters. Hydrophytes and hygrophytes of Sardinia. PASQUALE MOLA. *Atti accad. sci. Torino* **54**, 478–502(1918–19); *Botan. Abstracts* **4**, 159.—The first part of the paper deals with the ecological factors of the places explored, showing the influence, of altitude, chem. compn., source and rapidity of flow of water, different soil water levels and wind in producing the vegetation characteristic of the area under consideration: an aquatic formation rich in hydrophytes and hygrophytes. The second part is a catalog of the orders and species of both cryptogams and phanerogams. H. G.

The behavior of wood and tree lichens on a limestone substrate. E. BACHMANN. *Ber. deut. botan. Ges.* **36**, 528–39(1918); *Botan. Abstracts* **4**, 213.—In the metabolism of endo- and epido-lithic lichens acids are secreted which form sol. salts with the limestone. The secretion of the acid is most pronounced on the surface of the gonida and the tips of the hyphae which penetrate the limestone formation rapidly. The nature of the acid is not known; however, it is very likely that it is H_2CO_3 which is liberated in the process of respiration of the organism. H. G.

The so-called hereditary substances and their localization in the plant cell. G. TISCHLER. *Biol. Zentr.* **40**, 15–28(1920); *Botan. Abstracts* **7**, 142.—Résumé of literature on compn. and behavior of chromosomes in relation to their function as bearers of Mendelian hereditary factors. A discussion is given of their chem. compn., cytological behavior and their role in heredity. H. G.

Studies on some plant galls in Japan. IPPO SIMBO. *Bot. Mag. Tôkyô* **33**, 1–12 (1919); *Botan. Abstracts* **3**, 424.—S. describes the galls on *Rhus javanica* caused by insects (*Schlechtendalia* sp. and *Nurudeopsis* sp.). He considers their classification and their morphological and histological characters as well as their development. Starch, sugar, fat, a trace of volatile oil, and considerable quantities of tannin are found in the galls, while albumin and Ca oxalate can be demonstrated only in early stages of their development. H. G.

Deastringency in the fruit of Diospyros kaki. YOSHICHIKA TOKUGAWA. *Bot. Mag. Tôkyô* **33**, 41–4(1919); *Botan. Abstracts* **3**, 422.—Astringency of unripe persimmons is due to the existence of tannin as a jelly-like substance in idioblasts of fruit. When ripening occurs astringency decreases and finally disappears, and the fruit becomes sweet. Loss of astringency is the result of hardening of the jelly-like content of the idioblasts so that the tannin becomes insol. in saliva; it is not the result of the removal or oxidation of the tannin. The tannin found in persimmons is coagulated into jelly by formalin, HCl, or H_2SO_4. H. G.

Some solution cultures of wheat without potassium. KOICHI MORITA AND BURTON E. LIVINGSTON. *Botan. Mag. Tôkyô* **34**, 71–90(1920); *Botan. Abstracts* **7**, 193.—Nutrient solns. without K produced very satisfactory growth of wheat seedlings for 3 weeks. About 90 different three-salt solns. were used in which the total concn. of the salts corresponded to about one atm. of osmotic pressure. All of these solns. were without K, and of these the ones with the lower concns. of the di-hydrogen phosphate produced the best plants. H. G.

The behavior of ash substances and nitrogen in autumn leaves. AUGUST RIPPEL. *Jahresber. Ver. angew. botan.* **16**, 122–32(1918); *Botan. Abstracts* **7**, 307–8; cf. *C. A.* **15**, 1554.—On the basis of his expts. R. does not believe in the theory of the conservation to the plant of the K, P, and N compds., held by some investigators as the explanation of the recession of these compds. during the yellowing of the leaves in the fall. He thinks the reason for the early recession (even before yellowing) of K from the leaf to the plant is to fulfill some, at present, unknown function and that the later recession of P and N is due to the fact that during yellowing of the leaf the transfer of substances from the leaf to the plant far outbalances the flow into the leaf of such substances. H. G.

The carbon dioxide assimilation of cultivated plants. VORNEMANN. *Mitt. deut. landw. Ges.* **35**, 302–3(1920); *Botan. Abstracts* **6**, 131.—This is a semi-popular paper setting forth especially the value of the CO_2 that is developed in the soil by the decay of org. matter and reaches the surface below the leaves of the growing crop. The practical conclusion is reached that fertilizer or green manure should be so applied as to produce the max. decay during the height of the growing season. The value of tillage consists partly in encouraging the evolution of CO_2. H. G.

Waage's phytochemical synthesis of phloroglucinol from glucose. M. NIERENSTEIN. *Nature* **105**, 391(1920); *Botan. Abstracts* **7**, 196.—N. has tried the expt. (floating leaves in sugar solns. exposed to sunlight) nearly 80 times in the last 15 years without success. H. G.

Excretion and its importance in plant life. KARL GERHARDT. *Naturwissenschaften* **8**, 7–8(1920); *Botan. Abstracts* **6**, 119; cf. *C. A.* **15**, 2899.—The work of Benecke, Amar, and especially Stahl has shown that the oxalic acid formed in respi-

ration and possibly in assimilation neutralizes the surplus (harmful) Ca in the plant. This explanation of the role of oxalic acid has contributed much to a new understanding of the exudation of water by the plant. This explanation of guttation, as developed mainly by Stahl, is discussed at length. H. G.

Laboratory experiments on the sprouting of potatoes in various gas mixtures. (Nitrogen, oxygen and carbon dioxide.) FRANKLIN KIDD. *New Phytol.* **18**, 248–52 (1919); *Botan. Abstracts* **5**, 135.—The following conclusions are reached: "(1) O is harmful to the potato tuber in concns. above 5–10%. O (80%) kills in 4 to 5 weeks. O (5–10%) is the optimal concn. for sprouting. (2) The harmful action of O is increased in the presence of CO_2. (3) CO_2 inhibits sprouting in a concn. of 20%. This concn. is at the same time harmful to some extent. (4) Higher concns. of CO_2 cause marked injury and death." H. G.

Comparative chemical analyses of Johnson grass seeds and Sudan grass seeds. GEO. T. HARRINGTON. *Proc. Assoc. Official Seed Analysts* **1919**, 58–64; *Botan. Abstracts* **5**, 157.—A brief account of the results of comparative microchem. and permeability studies, also, gross chem. analyses of the seeds of these two closely related grass plants are given. These studies were made to det. whether there are any differences in their chem. nature, which might serve as a basis for explaining their marked difference in dormancy, germinating and after-ripening. H. G.

The occurrence of methyl *l*-inositol in an Australian poisonous plant. J. M. PETRIE. *Proc. Linnean Soc. N. S. Wales* **43**, 850–67(1918); *Botan. Abstracts* **5**, 110–1. —*Heterodendron oleaefolium* Desf. (Sapindaceae), a large, drought-resistant shrub, endemic to Australia, was found to be strongly cyanogenetic. It contains the methyl ester of *l*-inositol; the method of extn. and characteristics and properties of the compound are given in detail. The amt. isolated was equiv. to 0.65% of the dried (at 100°) leaves. It is not optically isomeric with pinitol of Maquenne, which is the methyl *d*-inositol, possessing a different m. p. and optical rotation. It is apparently identical with Tanret's quebrachite and has been previously recorded for 3 plants only—*Aspidosperma quebracho* (Apocyanceae), *Hevea brasiliensis* (Euphorbiaceae) and *Grevillia robusta* (Proteaceae). The occurrence of this compd. is exceedingly rare, in contrast to the inactive inositol which exists as a plastic substance in most plants. *Heterodendron* also contains a cyanogenetic glucoside. H. G.

Hydrogen-ion concentration and other factors affecting the distribution of Fucus. FLOYD W. GAIL. *Pub. Puget Sound Biol. Sta.* **2**, 287–306(1919); *Botan. Abstracts* **5**, 131.—The H-ion concn. of the sea water is an important factor in distribution. The most favorable p_H is 8.0–8.2. At p_H 8.8 all growth ceases except the germination of oöspores. Likewise in seawater of p_H 6.6 (and lower exponents) growth is insignificant or wanting, except in young plants, especially in temps. above 17°. Temp. is, therefore, another detg. factor. Of the ranges tried, the lowest, 10.5 to 13°, was the most favorable. When the temp. was permitted to rise to 30° for a part of the time, the growth was almost or wholly stopped. In the presence of much *Ulva* the p_H of the surrounding water is raised too high for *Fucus*. In tide pools the extremes of both temp. and p_H are too great. Both desiccation and light are also important factors. H. G.

Bay trees (Pimenta acris). W. ROBSON. *Rept. Agr. Dept., Montserrat* **1917–18**, 17; *Imp. Dept. Agr., Barbados* **1919**; *Botan. Abstracts* **5**, 111.—A record is given of the yield of Bay leaves and oil from a plot for 7 consecutive years. The results of 41 distns. during 1917 are given. From these it was found that the av. *phenol* content was 55%, being 5% higher than the av. for 1914–16. H. G.

Ajowan plant (Carum copticum). W. ROBSON. *Rept. Agr. Dept., Montserrat* **1917–18**, 19–22; *Imp. Dept. Agr., Barbados* **1919**; *Botan. Abstracts* **5**, 111.—Interesting

cultural and distn. trials are recorded with this plant. The percentage of oil in the seed was found to be 3, while the % *thymol* in the oil is given as 40 to 45. H. G.

American horsemint (Monarda punctata). W. ROBSON. *Rept. Agr. Dept., Montserrat* **1917–18**, 22–3; *Imp. Dept. Agr., Barbados* **1919**; *Botan. Abstracts* **5**, 111.—Small trials with this plant gave satisfactory results, the oil obtained from distn. contg. about 44% by wt. of *thymol*. H. G.

The stimulating action of copper sulfate on plants. LUIGI MONTEMARTINI. *Rev. patol. veg.* **10**, 36–40(1920); *Botan. Abstracts* **7**, 204.—Tests were made by spraying one side of a plant and leaving the other unsprayed. When half of the leaves were treated in the morning with a dil. $CuSO_4$ soln. and removed in the evening, measured, and the dry wt. detd., it was found that the treated leaves had a greater dry wt. per unit area. When the leaves were treated at night and removed in the morning, they had a lower dry wt. per unit area. This indicates that the treatment stimulated the formation and translocation of org. matter. H. G.

Vegetable fats and oils. III. Drying oils. M. RINDL. *S. African J. Ind.* **3**, 256–65(1920); *Botan. Abstracts* **6**, 213.—A description is given of the sunflower, mainly in reference to its oil. The culture, soil preferences, varieties, harvesting, and utilization are discussed, and analyses of South African grown seeds are given. The culture of the plant in Rhodesia is also discussed in reference to effect of fertilizers, and use as a rotation crop with maize. Some com. data regarding sunflower seeds are included. Brief notes are also added concerning *Madia sativa*. H. G.

Exudation of water by Colocasia antiquorum. MARGARET G. FLOOD. *Sci. Proc. Roy. Dublin Soc.* **15**, 505–12(1919); *Botan. Abstracts* **5**, 117.—An inquiry into the question of whether the water exuded from the leaf tips of *Colocasia* was conduction water, or whether it was secreted from a special gland. The conclusions from the observations and expts., made when the soil about the plant was damp and the air satd., are that no gland or epithem functioning in secretion is present in the leaf tip. The phenomenon must depend upon the normal transfer of water through the plant. H. G.

Determining dry matter in root crops. SELMAR LOFT. *Seed World* **7**, 21–2(1920); *Botan. Abstracts* **7**, 95.—L. gives the testing methods used by Danish seed growers to obtain the desired results. Dry-matter detns. are described in detail, giving the methods of drawing samples, washing, and sawing the roots, and the treatment of the final samples. H. G.

Studies of inflated fruits. OTTO BAUMGÄRTEL. *Sitz. Akad. Wiss. Wien* **126**, 13–40(1917); *Botan. Abstracts* **4**, 230.—The bladder fruits (pneumatocarpien) of *Astragalus cicer* L., *Colutea halepica* Lam., *C. orientalis* Mill., *Nigella damascena* L., *Staphylea bumalda* D. C., and *S. pinnata* L. were studied from an anatomical and physiol. standpoint. These inflated fruits contain a higher atm. pressure than the surrounding air, which is thought to be the result of carbohydrate respiration within the unripe fruits. The inclosed gas, which may arise largely from certain tissues in some species and from different tissues of the fruit in other species, has a higher CO_2 content than the outside air. It is suggested that the biologic role of the inclosed atm. is to supply a moist medium around the developing seeds and also to aid in the development of a structure which will make wind dissemination of the fruit possible. A bibliography is given. H. G.

Cellulosic residue of leaves. A. J. J. VANDEVELDE. *Bull. soc. chim. Belg.* **29**, 317–22(1920).—The insol. cellulose residue (residue remaining after an acid and alkali treatment of the dried and powdered substance) of various leaves, including the vine, lilac, gooseberry, raspberry, and lime, at various periods of growth, was detd. Markedly irregular variations were found at different periods, and in different years, for the same kind of leaf, and no general relationships were apparent similar to those previously

found for the ash, water or starch content at different stages of development of the leaf. The acid residue and the alk. residue of the dried leaf showed analogous variations
J. S. C. I.

Use of colored screens for combating cryptogamic diseases of plants. R. LANCE. *Compt. rend.* **172**, 1201(1921).—The spray is prepd. by mixing 650 g. of ultramarine blue, 250 g. of ultramarine green, and 100 g. of ultramarine violet with several l. of water, adding 2 kg. of $CaSO_4$ and 1350–1400 g. of quicklime, and when the coloring is uniform, stirring in 1 kg. of $Al_2(SO_4)_3$ or 1.5 kg. of alum. The pptd. alumina fixes the dye and the whole mixt. is dild. to 400 l. and is ready for use. The deposit formed on the plants by the use of this spray acts as a color screen, permitting only blue, violet, and ultra-violet rays to pass. J. S. C. I.

Contributions to the flora of Western Australia. D. A. HERBERT. *J. Proc. Roy. Soc. W. Australia* **6**, 105–7(1919–20).—The flowers of *Boronia tenuis*, Benth. are pink in the field but the petals become blue on drying. The pink can be restored by HCl or in an atm. of moist CO_2 and the blue again produced by NH_3. The change of color is attributed to loss of CO_2 from the living petal on drying. Similar changes occur in flowers of other *Boronias* and *Eriostemons* on treatment with NH_3 and HCl but the mere loss of CO_2 does not affect their color. ALBERT R. MERZ

Experiments on root juices. I. Behavior with ferric solutions. GIULIO MASONI. *Staz. sper. agrar. ital.* **52**, 569–83(1919).—The root juices of various kinds of plants under similar conditions behave differently with a 1–2% $FeCl_3$ soln. since the Fe may undergo no, a partial or almost total flocculation and pptn. Where the formation of a ppt. is most rapid and abundant the substitution of ferric citrate for the $FeCl_3$ or the addition of citric acid or di-K citrate to the $FeCl_3$ prevents pptn. The addition of AcOH, NaOAc, or HNO_3 does not prevent pptn. (0.1 *N* solns. up to 2 cc.). Sugars are only weakly active in obstructing pptn. Citric acid has a min. limit where its effect is zero, the other acids have a max. limit at which they hinder pptn. Of the plants chicory, lupine, corn and carrot the root juice of the carrot keeps the Fe in soln. best. Next in order come lupine and corn. An ext. of corn stalk (in flower) shows a behavior similar to that of corn root juice. Pptn. of the Fe is not due chiefly to tannins but to all the colloids, to the proteids and perhaps also to the phosphates present in the juice. Particular substances will prevent the formation of the insol. ferric compd. M. thinks that chlorosis and, in general, conditions showing a deficiency of nutrition in plants are connected with similar phenomena in living plants. ALBERT R. MERZ

The effect of the conductivity of the air on photosynthesis. MARGUERITE HENRICI. *Arch. sci. phys. nat.* **3**, 276–90(1921).—Alpine plants and those from the plain were grown in ionized air and in air free from ions. Thoria was used to ionize the air, and the plants were protected from α-rays by sheets of Al. With low light intensity ionization favors photosynthesis. With higher light intensities ionization has no effect. The effect is noticeable at higher light intensities with Alpine plants than with those from the plain. The partial pressure of CO_2 acts in much the same way as light intensity. Ordinary variations in temp. have little effect. Rates of photosynthesis in ionized air 1.5–4 times that in unionized air were obtained frequently. No theory is advanced, but it is thought possible that the elec. condition of the plant is changed in such a way as to modify the rate of movement of ions in the cell juices. T. G. P.

The natural synthesis of vegetable products. T. G. H. JONES. *Chem. Eng. Mining Rev.* **13**, 324–5(1921).—An abstract of a paper on the general nature of chem. changes in plants. T. G. PHILLIPS

The occurrence of crystals of calcium sulfate in the Tamaricaceae. HERMANN BRUNSWIK. *Sitz. Akad. Wiss. Wien. Abt.* **1**, 129, 115–36(1920).—Crystals of $CaSO_4$ are especially abundant in the leaves and young stems of members of this family of

plants. The crystals were identified microchemically, macrochemically and crystallographically. The distribution of the crystals in members of four genera of the family is tabulated. No Ca oxalate occurs. In the very closely related families Fouquieraceae and Frankeniaceae, Ca oxalate is found, but no $CaSO_4$. T. G. PHILLIPS

Internal secretions in plants. P. C. VAN DER WOLK. *Umschau* **25**, 426–8(1921).—The idea of internal secretions as antitoxins is carried over to the resistance of plants to fungus and bacterial diseases, and to the toxic products of the metabolism of the plants themselves. T. G. PHILLIPS

High-polarizing beets and their progeny (URBAN) **28.** Mustard oil in plants (CAUDA) **17.** The polyoses of rotted beets (VOTOCEK) **10.**

E—NUTRITION

PHILIP B. HAWK

NORMAL

Vegetable milk of the soy bean in alimentation and in the therapy of gastro-enteric diseases of infants. ALBERTO MUGGIA AND ENRICO GASCA. *Gazz. Ospedali clin.* **42**, 356–58 (1921).—A suspension of soy-bean flour can be prepd. which is stable, and which has a nutritive value closely approaching to that of cow milk. Comparative analyses are given. To prepare a l. of "vegetable milk," 150–160 g. of the beans are steeped in tepid water for 12–24 hrs., which causes considerable swelling. They are then carefully crushed, 1 l. of water is added, little by little, and the whole then boiled 15 min., and filtered through sterilized gauze, forming a white emulsion. If the taste is not agreeable it can be improved by the addition of a small amt. of real milk. The suspension coagulates under much the same conditions as real milk, and similar precautions in its handling must be observed. Figures are given showing marked improvement and gain in wt. of infants in whose diet the suspension was substituted wholly or in part for true milk. This was especially noticeable in gastrointestinal disorders, or where human or cow milk was not well tolerated. "What is most important from our point of view, is that the soy-bean milk, in the cases observed by us, shows itself to be more easily tolerated than the milk of animals, and sometimes more easily than human milk. The expts. will be continued on a larger scale and under more exact biochem. control, and we believe that we shall be able to show that in many affections of the digestive system of infants where there is evidence of intolerance toward animal milk, we shall be able to substitute the soy-bean milk wholly or partially, not only without inconvenience, but with improvement in the local condition of the digestive organs, and improved general condition of the child." The use of soy-bean flour in prepg. food for diabetics, industrial uses of the oil, and of the "vegetable casein" are also suggested. References to the literature are given. H. W. B.

Some remarks on the elements of diet in infancy, with special reference to the employment of Czerny and Kleinschmidt's butter flour mixture. J. P. CROZER GRIFFETH AND A. GRAEME MITCHELL. *N. Y. Med. J.* **114**, 137–45(1921).—The authors review in part the literature concerned with the digestion and action of the different ingredients of the infant's diet and particularly the reports having to do with the feeding of the Czerny-Kleinschmidt butter-flour mixt. (*Jahrb. Kinderheilk.* **1918**, 87, 1). Their results lead to the conclusion that the feeding of this mixt. to infants often results in a better fat tolerance of the subjects than can be obtained by any other known method; and that they indicate a strong proof of the great need of the infant economy for a food sufficiently high in fat. F. S. HAMMETT

Unemphasized essentials of infant feeding. JESSE R. GERSTLEY. *N. Y. Med. J.* **114**, 160–2(1921).—Of clinical interest. F. S. HAMMETT

Artificial feeding of normal infants. WILLIAM L. ROST. *N. Y. Med. J.* **114,** 172–4(1921).—Advocates whole milk dilns. on caloric basis for infant feeding. F. S. H.

The mechanism of vitamine action. D. GANASSINI AND P. MANCINI. *Bull. gén. Thérap.* **171,** 125–33(1920); *Endocrinology* **4,** 457.—A brief review of the physiol., pathogenic and therapeutic action of the vitamines in which the opinion is expressed that their physiol. role is to regulate trophic exchanges in synergic connection with the trophic regulatory function of the products of the glands of internal secretion. H. G.

Differential dialysis of the antineuritic and antiscorbutic factors. S. S. ZILVA AND MASATARO MIURA. Lister Inst. *Biochem. J.* **15,** 422–26(1921).—Brown (*Biochem. J.* **9,** 591(1915)) has shown that if air-dried collodion membranes, which are highly impermeable, are placed in solns. of alc. and water they become permeable, the permeability increasing with the increase in the concn. of the alc. employed. Z. and M. dialyzed their material through collodion membranes which were prepared as follows: a 14% alc.-ether soln. of collodion, (356 A/9) supplied by the Necol Industrial Collodion Ltd., was introduced into a test-tube 14 cm. long and 3 cm. internal diam. The collodion was then either centrifuged or allowed to stand for about 12 hours in order to permit the bubbles of air to rise to the surface, the opening of the tube being protected by an outside tube in order to obviate the evapn. of the solvents. The tubes were inverted and the collodion was allowed to drain for 5 min. after which time the tube with the collodion was immersed in water and the thimble was stripped off. It was then washed in water, dried for 24 hrs. in the air and soaked for 24 hrs. in the alc.-water soln. of the requisite strength. After washing, the thimbles were kept in water until required for use. Autolyzed yeast was used as the source of the antineuritic vitamine. Vitamine B failed to diffuse in any appreciable extent through a membrane that had been soaked in 90% alc. (90% membrane), but did so entirely through a 95% membrane. Similarly, vitamine C (obtained from lemon juice, from which the citric acid had been removed by means of $CaCO_3$) failed to pass through a 90%, but did through a 95% membrane. "The antineuritic and the antiscorbutic accessory factors diffuse through a collodion membrane of such permeability as permits the passages of substances like methylene blue, neutral red and safranine. It is suggested that the active mols., whether simple or associated, may be of a semi-colloid nature." BENJAMIN HARROW

Studies in nutrition. VII. The nutritive value of the proteins of tomato-seed press cake. A. J. FINKS AND C. O. JOHNS. Bur. of Chemistry. *Am. J. Physiol.* **56,** 404–7(1921).—White rats fed rations in which all the protein (18.4%) was supplied by tomato-seed press cake grew at the normal rate. Water-soluble B and fat-soluble A vitamines apparently were furnished in adequate amts. for normal growth when one-half the ration consisted of tomato-seed cake, the other half being made up of purified products. J. F. LYMAN

Studies in nutrition. IX. The nutritive value of the proteins from the Chinese and Georgia velvet beans. A. J. FINKS AND C. O. JOHNS. Bur. of Chemistry. *Am. J. Physiol.* **57,** 61–7(1921).—Velvet-bean meal, steam cooked or autoclaved and supplemented with either cystine or casein, led to nutritional failure in white rats. There was lack of growth, regurgitation, diarrhea and untimely death. The isolated proteins, coagulated by heat, were adequate for nutrition, but the dialyzed isolated raw proteins were not so. An associated toxic substance seems the most probable source of the disturbances. The coagulated isolated proteins of the velvet beans were about twice as well digested as the raw dialyzed isolated proteins. J. F. LYMAN

The effect of cooling power of the atmosphere on body metabolism. J. A. CAMPBELL, D. HARGOOD-ASH AND LEONARD HILL. *J. Physiol.* **55,** 259–64(1921).—Basal metabolism of the body cells is raised by outdoor conditions. Cooling power of the

atm., not temp., controls metabolism. Out-of-doors the cooling power is increased. Shivering is not necessary for increased metabolism. J. F. LYMAN

Vitamines and certain aspects of their relation to public health. J. C. DRUMMOND. Univ. of London. *Am. J. Pub. Health* **11**, 593–7(1921).—Classification of these substances and speculation as to their action is not only useless but dangerous until lab. expts. have solved the problems by accurate methods. D. warns against the com. exploitation of vitamines. Natural sources for these products abound on every hand. NATHAN VAN PATTEN

The role of glucosides in biology. A. GORIS. *Rev. gén. sci.* **32**, 337–42(1921).—An excellent review. G. supports the view that glucosides are excretory products. Their nutritive value is incidental and due entirely to the glucose formed by their hydrolysis. On hydrolysis the nonsugar may be oxidized, yielding compds. that are not toxic to the plant. T. G. PHILLIPS

The influence of calcium and phosphorus in the feed on the milk yield of dairy cows. EDWARD B. MEIGS AND T. E. WOODWARD. Bur. Animal Ind. U. S. Dept. Agr., *Bull.* **945**, 1–28(1921).—Feeding cows for several years according to the commonly accepted standards with little or no additional pasture may result in their milk yield being reduced much below the optimum. Results obtained in an exptl. investigation indicate that this condition is due to an insufficiency of either Ca or P or both in their rations and that it may be corrected by giving the animal a dry period of 2 months and feeding during that period a ration containing legume hay and grain with a high P content and with 3–4 times the amt. of protein required for maintenance and 2–3 times the total nutriment. W. H. ROSS

The utilization of calcium compounds in animal nutrition. E. B. FORBES, G. O. HALVERTON, L. E. MORGAN, J. A. SCHULZ, E. B. WELLS, C. H. HUNT AND A. R. WINTER. Ohio Agr. Expt. Sta., *Bull.* **347**, 99 pp.(1921).—The investigation is a study of the metabolism of growing swine on cereal rations as affected by supplementary additions of (1) pulverized limestone, (2) bone flour, (3) raw rock phosphate floats and (4) $CaCO_3$. Characteristics of the metabolism of swine on a ration of corn, oil meal and wheat middlings and NaCl were loss of Ca, subnormal retention of Mg and P and high acidity and ammonia of the urine. The feeding of lime material caused marked increase in Ca, Mg, and P retention. The carbonate prepns. lowered urinary acidity and NH_3 while pptd. bone flour increased these products. Of the Na excreted about $^1/_3$ was contained in the urine and $^2/_3$ in the feces. A still larger proportion of K was eliminated in the feces. Pptd. $CaCO_3$ and steamed bone produced relatively dense and strong bones, while rock phosphate produced bones slightly more dense and not quite so strong as did unsupplemented ration. Pptd. bone was intermediate in this regard. In rock phosphate floats fed swine there was a higher proportion of P to Ca than in other lots. Rock phosphate produced no greater strength of skeleton in relation to live weight than did a ration without mineral supplement. Steamed bone, pptd. bone flour, pulverized limestone and $CaCO_3$ caused marked increase in strength of the bone. Steamed bone produced bones contg. less moisture and fat and more ash than did other treatments. The Ca and CO_2 contents and hardness of the bone excelled other lots, while the Mg content was the lowest. Bones of pigs raised on a cereal ration without a mineral supplement were relatively poor in mineral constituents other than Mg. The hardest bones were characterized by the max. per cent of Ca, CO_2, and ash and min. Mg content. The softest bones were characterized by max. proportions of Mg and P and min. proportions of Ca and CO_2. J. J. SKINNER

ABNORMAL

The treatment of nutritional disorders in artificially fed infants. CHARLES HERRMAN. *N. Y. Med. J.* **114**, 158–60(1921).—Of clinical interest. F. S. HAMMETT

Diabetes mellitus and war diet in Vienna. H. ELIAS AND R. SINGER. *Deut. med. Wochschr.* **46**, 561–2(1920).—In Vienna, as well as in Berlin, the underfeeding incident to the war has had a good influence on diabetes. There are, however, differences. In Berlin the patients showed glucemia even when the urine was sugar-free; in Vienna, when there was no glucosuria the amt. of blood sugar was lower than normal. In Vienna, elderly patients with diabetes during the war were in better condition than young patients. The good influences of underfeeding most probably are to be attributed to the small quantities of proteins ingested. H. G.

The maintenance diet in diabetes mellitus as determined by the nitrogen equilibrium. H. O. MOSENTHAL. *Trans. Assoc. Am. Physicians* (Phila.) **32**, 159–71(1917); *Endocrinology* **3**, 361.—Metabolic studies on 9 diabetics are reported. It was found that patients could be established in N balance by a protein-fat diet having a caloric value equal to the standard caloric requirement. In many cases N equil. is possible at a sub-standard caloric level. The factors detg. the minimal level at which balance can be maintained are apparently very numerous and partially unknown, but glucosuria and slight infections are two that may necessitate an increased food intake to avoid a N deficit. It is necessary to maintain N equil. if the physical and mental efficiency of the patient are to be conserved. On a carbohydrate-free régimé this amts. roughly to 1500–2000 calories, women and smaller individuals in general requiring less than normal size men. A positive N balance may be attained in diabetics while on carbohydrate-free diet. H. G.

The basal metabolism and the specific dynamic action of protein in liver disease. JOSEPH C. AUB AND JAMES H. MEANS. Mass. Gen. Hosp. and Harvard Univ. *Arch. Intern. Med.* **28**, 173–91(1921).—"The basal metabolism in 12 cases of liver disease (gallstones, cirrhosis, carcinoma, acute catarrhal jaundice) was essentially within normal limits. The liver is, therefore, either not an important regulator of the metabolic rate, or it is adequate for this purpose even when severely diseased. The rate of absorption and utilization of protein in large quantities was usually normal, even in severe cirrhosis. In 2 cases of cirrhosis and one of gallstones, the utilization of the protein was delayed or absent. Marked portal obstruction caused no delay in the appearance of the specific dynamic action of protein. The cases of cirrhosis showed, on the whole, the highest metabolic response to protein katabolism. The conclusion seems justified that either the liver is not the main site of the specific dynamic action of protein, or that it can adequately perform that function even in disease. The specific dynamic action of protein results from an increased combustion of protein and carbohydrate, rather than of fat. The observations of Du Bois (*C. A.* **10**, 2102), that in exophthalmic goiter a normal increase in heat production, due to protein, is superimposed on the high basal rate, is confirmed." I. GREENWALD

Phenols in the urine in pellagra. M. X. SULLIVAN AND PAUL R. DAWSON. U. S. Public Health Service. *Arch. Intern. Med.* **28**, 166–72(1921).—Analyses by the methods of Folin and Denis (*C. A.* **9**, 3263) indicated that there is, in the urine of pellagrins, little change from the normal, either in amt. of total phenols or in % of conjugation. Of 12 cases tested for indican, 10 gave a marked reaction. I. G.

Metabolic studies in a case of diabetes insipidus. I. M. RABINOWITCH. Montreal Gen. Hosp. *Arch. Intern. Med.* **28**, 355–66(1921).—The observations were made on a man, 47 yrs. old, in whom the condition had first been noticed a month previously. "Röntgenogram of skull shows no abnormality of the pituitary fossa, except that the fossa is shallow and the clinoid processes are indistinct. Sphenoidal sinus clear." The basal metabolism was normal and was not increased to an abnormal degree by the administration of thyroxin. "A diminished sugar tolerance was demonstrated, suggesting hyperfunction of the pituitary gland, and hypofunction of the suprarenals was suggested

by subnormal response of the basal metabolic rate to epinephrine and negative Csepai, Goetsch and Ascoli tests." On the ordinary hospital diet, with unrestricted fluid, the vol. of day urine was 2645 cc., of night urine 1600 cc. On the Mosenthal test diet, the sp. gr. of some specimens was as high as 1.020 and the night urine was normal in vol. and in concn. of N but was low in NaCl. Plasma NaCl was found to be 6.28 g. per liter and the blood urea N was 16.1 mg. per 100 cc. These figures were not increased by the ingestion of 20 g. NaCl or of 10 g. urea. I. GREENWALD

Effects of an unbalanced diet in the production of guinea-pig scurvy. G. M. FINDLAY. Royal College of Physicians' Lab. Edinburgh. *Biochem. J.* **15**, 355–7 (1921).—Four groups of guinea pigs received, resp., (1) a basal diet of oats and bran *ad libitum* with the addition of 60 cc. of autoclaved milk per diem; (2) the same diet as (1) plus 10 g. of caseinogen that had been autoclaved for 120° for 2 hours; (3) same as (1) plus 10 g. of cane sugar per day; (4) the same as (1) plus 10 cc. of cod-liver oil. The date at which the first symptoms of scurvy appear are not much affected by an excess of protein, carbohydrate or fat in the diet. The most striking feature is the considerable loss of body wt. in the guinea pigs fed with excess of carbohydrate. The histological appearances found in the bones and joints of the animals which were given cod-liver oil were identical with those met with in other cases of acute guinea-pig scurvy, thus showing once again that the lack of vitamine A is in no way responsible for the lesions that occur in exptl. scurvy. BENJAMIN HARROW

Relation of the fat-soluble factor to rickets and growth in pigs. S. S. ZILVA, JOHN GOLDING, J. C. DRUMMOND AND K. H. HOWARD. *Biochem. J.* **15**, 427–37(1921).—Two pigs were fed on extd. dried milk, cream (cow milk), purified caseinogen and salt mixt., and two on the same diet except that for cream autoclaved olive oil was substituted. "The results of our expts. offer no definite information on the relation of the fat-sol. factor to the etiology of rickets. We are, however, of the opinion that if the deficiency of this factor alone bore the same relation to the etiology of rickets as that of the antiscorbutic and antineuritic factors to the etiology of scurvy and beriberi, we should have obtained a better differentiation in the rachitic condition in the two groups." BENJAMIN HARROW

Studies on the effects of thirst. II. Effects of thirst upon the growth of the body and of the various organs in young albino rats. TOKUYASU KUDO. Univ. Minn. *J. Exptl. Zoöl.* **33**, 435–61(1921); cf. *C. A.* **15**, 886.—Albino rats, 1 month old, may be held at const. body wt. for several weeks by a restricted amt. of liquid (milk) in a diet otherwise adequate for growth. Tolerance of thirst is progressive, less milk being required for maintenance as the expt. proceeds. The effects upon the body are as follows: The tail becomes elongated while the body length remains const.; a marked increase in wt. of the skeleton and a slight increase in the visceral group occurs. The musculature remains nearly const. in wt., but the integument suffers a slight loss and the "remainder" a marked loss of wt. The growth tendencies of young rats under these conditions correspond to those in rats of similar age which have been underfed, although exceptions are found in the testes and kidneys. These thirst experiments also show a general resemblance to those in adult animals with certain differences according to age and the type of inanition employed. CHAS. H. RICHARDSON

Significance of accessory foodstuffs from vegetables in the dietetic therapy of rickets. E. FREISE AND P. RUPPRECHT. *Med. Klin.* **17**, 16–18(1921).—Changes in the P and Ca balances were detd. in a well developed case of rickets following the administration of an ext. of carrots. The ext. was given, heated or unheated, daily for 5-day periods. During a preliminary test period the daily retention of P_2O_5 and CaO was 0.888 and 0.123, resp. In the 5-day period immediately following, the unheated ext. was given and the corresponding figures were 0.748 and 0.144. In a second test

upon the same child, conducted a month later, a greater effect upon retention of P_2O_5 and CaO was noted. With the heated ext. the P_2O_5 retention changed from 0.455 to 0.486 and the CaO from 0.275 to 0.293. Comparable detns. were made in normal children under the same exptl. conditions. G. H. S.

Experimental rickets in rats. I. A diet producing rickets in white rats, and its prevention by the addition of an inorganic salt. H. C. SHERMAN AND A. M. PAPPENHEIMER. Columbia Univ. *J. Exptl. Med.* **34**, 189–98(1921).—A diet of 95% patent flour, 3% Ca lactate and 2% NaCl or of 95% patent flour, 2.9% Ca lactate, 2% NaCl and 0.1% Fe citrate regularly induced rickets in young rats. The substitution of 0.4% K_2HPO_4 for a small part of the Ca lactate in the diet completely inhibited the development of rickets. Quant. detn. of Ca in the bodies of parallel rats showed a marked increase of Ca content in the rats receiving K_2HPO_4 over those which developed rickets. While it is thus shown by α-rays and by histological examn. and by quant. chem. analysis that added K_2HPO_4 increased the assimilation and normal deposition of Ca, it may be the quant. relationship between the inorg. ions rather than an actual deficiency of any one of them which was the detg. factor in the cause or prevention of rickets.

C. J. WEST

Vitamines of dried milk (STEPP) **12.**

F—PHYSIOLOGY

ANDREW HUNTER

Causes of variation of the zinc content of vertebrate animals. GABRIEL BERTRAND AND R. VLADESCO. *Bull. soc. chim.* **29**, 736–9(1921).—See *C. A.* **15**, 1922.

E. J. C.

The physiological chemical action of follicular extract. H. WINTZ. *Arch. Gynaecke* (Berlin) **113**, 457–71(1920); *Endocrinology* **5**, 372.—Among a great number of expts. carried out in the study of the internal secretion of the ovary a certain number were done in which the effects of the follicular ext. were tried on blood pressure, blood coagulation and local action on the genitals. With rabbits as the exptl. animals, small doses given intravenously caused a fall in blood pressure, while large doses gave the opposite reaction, though neither of the reactions was very marked. When the ext. was injected in the ear vein and blood taken two minutes later and tested for coagulation time, it was found that this phenomenon was slightly but significantly lengthened. No effect on the genitalia was observed. No effect of the ext. could be observed on the coagulation time of blood in man, nor was menstruation either augmented when slight or diminished when profuse, as the result of the injection of such exts. in 1.5 cc. amts. These expts. were all done when exts. from fresh tissue were used. When old tissue exts. were tried there was obtained a rise in blood pressure even with small amts., there was a shortening of blood coagulation which, however, was a transitory phenomenon, and no action on the genitalia was observed. When corpus luteum exts. were similarly studied they were found to produce a fall in blood pressure, a slowing of blood coagulation and an hyperemia of the genitalia. (This, however, only occurs after some 30 days' injections.) A review is then given of the action of lipamin and luteolipoid prepns. obtained from the corpus luteum. The former causes a slight drop in the blood pressure, while the latter has no effect. Lipamin retards the coagulation of blood, while luteolipoid accelerates it markedly. Moreover, luteolipoid but slightly accelerates the growth of the genitalia of virgin rabbits, while the lipamin effect on the uterus and mammae is most marked. Luteolipoid when injected during the menstrual period is an efficient inhibitor, save in those cases due to endometrial pathology. Lipamin when injected in patients with amenorrhea yields relief, but has no effect on a normally menstruating woman. H. G.

The hormonic function of lymphatic glands. P. MARFORI. *Arch. ital. biol.* **68,** 113(1918); *Endocrinology* **3,** 81.—M. extd. the mesenteric lymph glands with physiol. saline. He has shown that this ext. contains one or more active substances which are not destroyed by a temp. as high as 110°. In the dog and rabbit, injection of the above ext. caused a transitory fall in blood pressure and an increase in heart rate. It was shown to cause dilatation of the vessels through peripheral action by injection into a perfused limb. If atropine is given, the ext. causes a slowing of the heart instead of acceleration. The isolated coronary artery is constricted by the ext. as is the pupil of the enucleated frog's eye. M. has found that this ext. antagonizes the action of adrenaline in the heart, blood vessels and iris and even states that it antagonizes adrenaline glucosuria. H. G.

The biochemistry of hypophysis, adrenal and thyroid glands. E. RICHTER. *Deut. med. Wochschr.* **45,** 709(1919); *Endocrinology* **3,** 533–4.—If to 6–10 cc. distd. water, 0.25 cc. of 1% soln. of adrenaline is added and raised to the b. p., and then 0.25–0.05 cc. of cold 1.1% soln. of Na-Au chloride is added, this salt is reduced and a red soln. of colloidal Au is formed. Thus it is proved that adrenaline has reducing properties. The reduction time may vary from 15 mins. to 8 days. Adrenaline soln. in acetone or alc. gives a similar reaction. R. believes that this reduction is precisely the opposite to oxidation in the lungs. He believes also that the pigmentation of the skin in Addison's disease is due to a failure of reducing power leading to oxidation of the normal pigment. R. has prepd. reducing substances also from the thyroid and hypophysis. Similar material can be obtained from the cerebrum, ovary and testis and, in traces, from the thymus. Reducing substances cannot be obtained from lymph glands, salivary glands, liver, kidney or cerebellum, it is stated. (The demonstration that certain gland substances have reducing power has little significance in the absence of proof that such are contributed to the blood stream. K. naively adds the information that the reductions reported take place satisfactorily only in acid solns., free from protein, conditions which are never present in the body.) H. G.

The blood sugar during a voyage from Holland to India. H. SCHUT. *Geneesk. Tijdschr. Ned. Indie* **60,** 424–9(1920); *Endocrinology* **5,** 104.—In the tropics the amt. of blood sugar is about 30% higher than in Holland. When people with this large quantity of sugar go on the mountains or make a voyage, the blood sugar becomes normal. The so-called "low fever" frequently observed in India may be considered as an effort of the body to oxidize the surplus of sugar. S. examd. the blood of people making a voyage from Holland to India. As long as they are on sea the amt. of sugar is not increased, even when they are in the tropical seas. It was possible to examine 3 mild cases of diabetes in all of which the glucosuria disappeared during the voyage. H. G.

Influence of flying on glucemia. G. MARAÑÓN. *Siglo Méd.* (Madrid) **65,** 573–4 (1919); *Endocrinology* **4,** 451.—In a series of tests made on aviators it was found that an increased glucemia resulted from the flying, caused by the emotional state induced. In the majority of cases the blood sugar values were increased from the normal of 0.09 to 0.12 to values represented by 0.15 to 0.19. In the pilots the hyperglucemia was less, but nevertheless values above the normal were found. H. G.

The nucleoprotein of the thyroid. W. GRÖBLY. *Mitt. Grenzg. Med. Chir.* **30,** 403(1918); *Endocrinology* **3,** 118.—Puppies show marked changes in the thyroid after administration of iodothyroglobulin or thyronucleoprotein. These are increase of colloid, atrophy of the epithelial cells and atrophy of the intervesicular tissue; the vacuoles shrink or totally disappear. In case of thyronucleoprotein feeding there is more marked epithelial atrophy and more affinity of the colloid for alc. stains than when iodothyroglobulin is used. Gröbly theorizes to the effect that the nucleoprotein dimin-

ishes the soly. of the colloid; hence the function of this material is to retain colloid in the gland; a deficiency of the nucleoprotein would lead, therefore, to increased resorption of the colloid and, hence, hyperthyrosis. In Graves' disease there is not only evidence of hyperthyrosis but also of diminished formation of nucleoproteins in general. This indicates a relationship between the thyroids and P metabolism. Hence in Graves' disease P should be administered. H. G.

Action of acetone extracts of duodenal mucosa upon arterial pressure and upon the pancreas. L. CERVERA. *Treballs soc. biol. Barcelona* **6**, 19–21(1918); *Endocrinology* **4**, 683–4.—Exts. of duodenal mucosa made with acetone were compared with those made with acidulated saline soln. as regards their effects upon blood pressure and pancreatic secretion. The acetone exts. were somewhat less active but produced a marked acceleration of pancreatic flow with no more than 10 mm. reduction of blood pressure. Hence secretin is not identical with Popielski's vasodilatin. C. suggests that the secretin acts on a "receptor substance" as postulated by Langley. H. G.

Nature of the reducing substance in human blood. E. A. COOPER AND HILDA WALKER. Univ. Birmingham. *Biochem. J.* **15**, 415–21(1921).—A careful review of Maclean's estn. of sugar in the blood (*C. A.* **13**, 2889) is presented. Neither uric acid nor creatinine in amts. larger than those normally met with in blood interfere with the method. In the attempt to answer the questions whether the reducing substance estd. by the Maclean method is entirely sugar or whether an interfering substance is present, and what is the nature of the sugar present, C. and W. show that the reducing substance is destroyed by boiling with ammonia and is insol. in ether, as is the case with reducing sugars. They also isolated phenylglucosazone from human blood; and they further conformed the observations of Pavy (*J. Physiol.* **26**, 282(1901)) and Cammidge (*C. A.* **14**, 3457) that the reducing power of blood increases after hydrolysis with HCl, indicating the presence of a hydrolyzable substance. BENJAMIN HARROW

Note on the oxygen consumption of amphibian muscle and nerve. N. K. ADAM. *Biochem. J.* **15**, 358–62(1921).—By means of A.'s instrument (cf. *C. A.* **15**, 1547) the rate of respiration observed in resting muscle was as follows: Sartorius muscles, 0.10 to 0.135 cc. per g. per hour, reduced to normal temp. and pressure; gastrocnemius muscles, 0.05 to 0.12 cc.; sciatic nerves, 0.05 to 0.08 cc. The Tashiro method for estg. small amts. of CO_2 (*C. A.* **7**, 3999, 3982) is criticized. BENJAMIN HARROW

Specific electrical resistance of frog muscle. WILLIAM HARTREE AND A. V. HILL. *Biochem. J.* **15**, 379–82(1921).—Working at various temps., the authors detd. the elec. resistance of a frog sartorius muscle, after death, to a single phase a. c. of about 90 periods per sec., and of a strength of the order of 1 milliamp. At all temps. the sp. cond. of the muscle is the same as that of a 0.36% NaCl soln. BENJAMIN HARROW

The distribution of calcium and phosphoric acid in the blood of normal children. MARTHA R. JONES AND LILLIAN L. NYE. Univ. Cal. Medical School. *J. Biol. Chem.* **47**, 321–31(1921).—"The alk. reserve of plasma and the distribution of Ca and the various compds. of H_3PO_4 in the blood were studied in 34 normal children whose ages ranged from 4 weeks to 14 years (17 boys and 17 girls). The blood corpuscles are richer in all types of H_3PO_4 compds. than plasma. The amt. of unknown H_3PO_4 in plasma is negligible, if any, while in corpuscles it averages approx. 70% of the total. In general, the values for boys averaged slightly higher than those for girls. The lipoid H_3PO_4 content of corpuscles averaged 17.7% higher in boys than in girls, while the plasma values in boys were 16.6% higher than in girls. The inorg. H_3PO_4 content of corpuscles showed the greatest % variation of all the P compds. of the blood. The av. Ca content of corpuscles was found to be slightly less than that of the plasma, the values in mg. per 100 cc. being as follows: whole blood, 9.4; corpuscles 8.7; plasma, 10.0. A relation between Ca and H_3PO_4 contents of the blood is not apparent. The CO_2-com-

bining power averaged 51.8 vols. % in 32 children. No relation between the alk. reserve and the concn. of Ca and H_3PO_4 in the blood can be established." A. P. L.

The relation of the migration of ions between cells and plasma to the transport of carbon dioxide. EDWARD A. DOISY AND EMILY P. EATON. Wash. Univ. Med. School. *J. Biol. Chem.* **47**, 377-93(1921).—Defibrinated beef blood was exposed to various tensions of CO_2 and the serum was analyzed for its Na, K, Cl, and P content and the bicarbonate concn. detd. by titration to a standard p_H of 7.2. The loss of Cl is equiv. to the gain in HCO_3 in serum so that for each mol. of HCl lost a mol. of $NaHCO_3$ is gained. No transfer of either Na or K from cells to serum occurs so that the blood cells are impermeable to both these cations. If any migration of PO_4 occurs (most of the results obtained were within the possible exptl. error), it is quant. of little importance in the transport of CO_2. There is a marked increase of corpuscle vol. with increasing CO_2 tensions, the osmotic pressure of the cell contents increasing more rapidly than that of the serum, owing to the HCl which is taken up by the cells and which interacts with the cell proteins. A. P. LOTHROP

The secretion of the pars, pylorica gastri. A. C. IVY AND Y. OYAMA. Loyola Univ., School Medicine. *Am. J. Physiol.* **57**, 51-60(1921).—The secretion of the pyloric antrum in dogs is mucoid, viscous, tenacious, transparent, odorless, and slightly salty in taste. It is slightly alk. with a p_H 7.00 to 7.50. It contains no substance that is of sp. digestive importance. The effect of various stimuli on secretion was studied. Analyses of 6 specimens in terms of g. per 100 cc. follows: total solids 1.33 to 2.42; total ash 0.558 to 1.54; total N 0.054 to 0.095; pptd. by alc. 0.896 to 1.12; total Cl 0.458 to 0.64; N as NH_3 0.0033 to 0.0054; amino-acid N 0.0023 to 0.0025; sp. gr. 1.008 to 1.011; Δ $-0.61°$ to $-0.64°$. J. F. LYMAN

Changes in concentration of the carbon dioxide resulting from changes in the volume of blood flowing through the medulla oblongata. A. B. HASTINGS, HELEN C. COOMBS AND F. H. PIKE. Columbia Univ. *Am. J. Physiol.* **57**, 104-9(1921).—When the vol. of blood flowing through the medulla oblongata is reduced by clamping blood vessels there is an increase in magnitude or rate of the respiratory movements, a marked rise of the arterial blood pressure, and a fall in arterial CO_2. It appears that conditions in the central mechanism itself det. respiratory activity. J. F. LYMAN

Is catalase a measure of metabolic activity? S. MORGULIS. College Med., Univ. Nebraska. *Am. J. Physiol.* **57**, 125-34(1921).—Frogs were kept at different temps., killed, the entire bodies extd. and the catalase of the ext. was detd. Exposure to widely different temps., such as would effect a change in metabolic rate of 300 to 400%, showed practically no difference in catalase content per g. frog. It is concluded that whatever the function of catalase in the organism may be, it is certain that it is not a measure of metabolic activity. J. F. LYMAN

Influence of glands with internal secretion on the respiratory exchange. II. Effect of suprarenal insufficiency (by removal or by freezing) in rabbits. D. MARINE AND E. J. BAUMANN. Montefiore Hospital. *Am. J. Physiol.* **57**, 135-52(1921); cf. *C. A.* **15**, 1752.—Removal or crippling by freezing of the suprarenal glands in rabbits causes a disturbance of metabolism, usually an increased heat production and CO_2 output. The disturbance appears definitely related to the completeness of removal of the cortical function. The symptom complex, both anatomical and physiol., resulting from the destruction of the suprarenal function in rabbits, resembles in many essential features that of exophthalmic goiter. J. F. LYMAN

The function of the urinary tubules in the frog. MILDRED ATKINSON, G. A. CLARK AND J. A. MENZIES. Univ. Durham, College Med. *J. Physiol.* **55**, 253-8(1921).—Perfusion expts. with frog kidneys, by using solns. contg. dextrose, sulfates and urea, show that all 3 are filtered through the glomerular membranes. The cells of the tubules

are capable of transmitting urea and Na_2SO_4, but not glucose, from perfusing fluid to urine. J. F. LYMAN

The regulation of the blood's alkalinity. II. J. B. S. HALDANE. Oxford. *J. Physiol.* **55,** 265-75(1921); cf. *C. A.* **15,** 2483.—Acidosis was produced in man by the ingestion of NH_4Cl (5 to 55 g.). The NH_4Cl passes rapidly from the digestive tract into the blood. Presumably in the liver a part of the NH_4Cl is converted into urea, the HCl liberated going to reduce the alk. reserve of the blood and tissues. The alveolar CO_2 falls, in one expt., from 39.1 to 27.4 mm. pressure. The blood CO_2 falls, in one expt., to 58.4% of the normal. The excretions of acid by the kidneys rises. All of these conditions occurring together prove that a true acidosis is produced. The lungs take the principal part in compensating for the blood disturbances in NH_4Cl acidosis, about 96% of the bicarbonate change of the blood being compensated for by the respiratory center. It was calcd. that in one expt. the kidneys eliminated 30% of the excess acid in 24 hrs. This contrasts unfavorably with the rate at which they can deal with excess alk. In acidosis there is an increase in urinary phosphates. The ratio of acid to NH_3 in the urine depends on the amt. of phosphates available for excretion. J. F. L

The coagulation of the blood. II. The plotting complex. H. W. C. VINES. *J. Physiol.* **55,** 287-95(1921); cf. *C. A.* **15,** 3313.—V. prepd. a mixt. of lecithin, nucleoprotein and $CaCl_2$, having marked coagulating powers against a fluoride blood, the Ca of the mixt. alone not being responsible for the coagulating effect. The theory is advanced that the inauguration of blood coagulation depends on the presence of a complex in which 3 substances are combined, lipoid, Ca, and a protein. The lipoid and the Ca are essential. The Ca-lipoid combination does not yield Ca ions. The function of the protein is apparently secondary, rendering the lipoid more sensitive or keeping it in a state of fine suspension. The lipoid-Ca complex has properties resembling those of the thrombokinase of Morawitz rather than of the prothrombin of Howell. J. F. LYMAN

The effects of respiration of oxygen on breathing and circulation. L. DAUTREBANDE AND J. S. HALDANE. Oxford and Lister Inst. *J. Physiol.* **55,** 286-9(1921).—Breathing O_2, particularly at increased barometric pressure, increases the breathing and diminishes the pulse rate. These effects are presumably brought about by slowing of the blood flow through the tissues, which protects them against the poisonous action of the high O_2 pressure. J. F. LYMAN

Liver, blood plasma and protein sugar. H. BIERRY AND F. RATHERY. *Compt. rend.* **172,** 1445-7(1921).—Laparotomy was performed on 3 large anesthetized dogs after a fast of 24 to 48 hrs. Samples of blood were simultaneously drawn from the femoral, superior mesenteric and suprahepatic veins, ligatures being placed at the last moment on the suprahepatic veins so as to avoid any reflux of blood from the right heart, diaphragmatic veins, or vena cava inferior. The samples were received in vessels containing NaF and immediately centrifuged. The water, free sugar, protein sugar and total protein were then detd. The protein sugar from the suprahepatic vein per 1000 cc. of water was 0.37, 0.93 and 0.61 g., resp.; the ratio of protein N to protein sugar was 13.3, 11.0 and 13.5, resp. The corresponding figures for the portal plasma were 1.22, 1.23 and 1.10 and for the ratio of protein N to protein sugar 7.3, 8.2 and 8.3, resp. These figures support the conclusion that the blood plasma undergoes a qual. and quant. modification in the liver, and that the liberation of sugar is at the expense of the plasma proteins. L. W. RIGGS

Compensating role of chlorides in its relations to the chemical composition of body fluids. W. MESTREZAT AND MISS LEDEBT. *Compt. rend.* **172,** 1607-10(1921).—The object of this study was to demonstrate by expt. that the chlorides intervene as compensating factors in the maintenance of the isotonic characters of the body fluids.

The partial or total sepn. of the colloids in the various plasmas was attained by filtration through collodion membranes under pressure. Sacs formed of 2 or 3 layers of collodion rich in cellulose, sterilized 10 min. at 110°, with a capacity of 40 to 50 cc., were filled with pure water or water containing 5 per 1000 of salt, and dialyzed against 700 to 800 cc. of fresh horse serum. The Cl content of the liquid in the sacs was followed by a microchem. method. The surrounding serum was renewed until a definite equil. with the original serum was established. The "equil. dialysates" obtained with the serum were colorless, isotonic, being deprived of albumin, and rich in Cl. Two out of 14 trials gave a dialysate containing 1.0 and 1.14 g., resp., NaCl per liter more than in the original serum. In 12 tests the ratio of NaCl in the dialysate to that in the serum ranged from 1.11 to 1.25. Similar results were obtained *in vivo*. The dog, rabbit and guinea pig supported the perfectly aseptic introduction into the abdominal cavity of a dialyzing app. consisting of a sterilized collodion sac containing a saline soln. 5 to 1000. The animals were killed 3, 6 or 15 days after the introduction of the sac. Ca, Mg and other elements also appear to take part in the compensation. L. W. RIGGS

G—PATHOLOGY

H. GIDEON WELLS

Function of the human adrenal cortex in normal condition and in infections, particularly gaseous gangrene. N. GOORMAGHTIGH. *Arch. méd. expl.* **28**, 277(1918); *Endocrinology* **3**, 345–6.—An extended study of the morphology of normal and pathological adrenals led to the conclusions that each zone of the cortex has a certain sp. function, and that the infections of a gangrenous type accompanied by gas formation cause a liberation of a considerable amt. of cholesterol and cholesterol esters into the blood stream with consequent disturbances of function. H. G.

Glucemia and adrenine hyperglucemia in the dove. G. MARAÑÓN AND A. ROSIQUE. *Bol. soc. españ. biol.* **1916**, June 10; *Endocrinology* **3**, 189–90.—Analysis by Bang's method gave an av. glucose content of the blood in normal doves of 0.080%. Adrenine injections constantly increased the percentage to about 0.09 or 0.10. Treating the doves with thyroid exts. did not augment the adrenine glucemia reaction as it has been reported by several observers to increase the vasomotor effects. H. G.

The physical state of the blood serum in relation to its agglutinin and antibody content: The effect of friction and pressure. C. J. BOND. *Brit. Med. J.* **1919**, 729–33; *Abstracts Bact.* **3**, 378.—A study of the effect of grinding on various sera in respect to hemagglutinin content with varying results, dependent upon the serum used. In one series of expts. the agglutinating titer of a polyvalent dysentery serum was increased. H. G.

Xanthoma diabetica. FAHR. *Deut. med. Wochschr.* **45**, 1373(1919); *Endocrinology* **4**, 292.—The diabetic xanthomas generally contain large quantities of cholesterol, but in the case described only traces of this compd. were found, the mass consisting almost entirely of neutral fat. The opinion is expressed that diabetic xanthoma is caused by lipemia with diminished lipolytic activity of the blood. H. G.

Some remarks on the blood sugar in diabetes mellitus. S. LINDBLOM. *Hygiea* **81**, 753–9(1919); *Endocrinology* **4**, 477.—In diabetes the ability to regulate the relation between production and consumption of sugar, so that equil. obtains without glucosuria, is arrested or destroyed. In this case there must of necessity be a higher blood sugar content than is compatible with the kidney permeability, so that the organs or eventually their centers react with a decreased production or an increased destruction. The hyperglucemia present in diabetics acts then in opposition to the metabolic disturbance. Hyperglucemia is then in a certain degree an advantageous symptom. According to this conception the urine of many diabetics does not become sugar-free in spite of the

residual hyperglucemia but because of it. The favorable action of the oat-cure is explained on the basis of the suddenly increased hyperglucemia. H. G.

Goiter and drinking water. B. D. G. KAPPENBURG. Inaugural Dissertation, Utrecht, 1919; *Endocrinology* **3**, 419.—A large number of expts. on rats is reported. K. concludes that the role played by drinking water in the etiology of goiter is still problematic and that, in fact, it is not proved that it plays any part at all. H. G.

The relation between blood pressure and blood sugar. C. HOVENS GRÉVE. Inaugural Dissertation, Leiden 1919; *Endocrinology* **4**, 238–9.—It is well known that adrenaline has an influence both on the blood pressure and on sugar metabolism. Increases in blood pressure after injection of adrenaline may be accompanied by glucosuria. On the other hand, the low blood pressure in Addison's disease is accompanied by a diminished amt. of blood sugar. Therefore the author examd. the blood in nephritis, in hypertonia without nephritis and in diabetes. In many cases no relation between blood sugar and blood pressure could be detected. There are, however, striking cases of hypertonia without demonstrable anatomical lesions with hyperglucemia. In diabetes there are two forms, those with and those without increased blood pressure. It is possible that this last form is of chromaffin origin. The treatment of these patients requires perfect psychic rest. Perhaps atropine or pilocarpine is of some use. When a patient has increased blood pressure and hyperglucemia one has, however, no right to speak of a "latent diabetes." The author proved that when a large amt. of carbohydrate was given to such a patient, the influence on the amt. of blood sugar was much smaller than when even a very small dose was administered to a true diabetic. H. G.

Cholesterolemia in diabetes. B. K. BOOM. Inaug. Diss. (Amsterdam) 1920; *Endocrinology* **5**, 248–9.—There is no relation between acidosis and the quantity of cholesterol in the blood plasma. In patients younger than 40, the amount of cholesterol is generally much higher than in older patients. No relation was found between the tolerance for carbohydrates and the quantity of cholesterol. Diet was noted to have no influence—even after prolonged fasting the cholesterol content may remain high. Similarly, no relation is found between xanthosis and cholesterol; the xanthosis is due, supposedly, to the high concn. of lipochrome in the plasma. Whether a high concn. of cholesterol is of bad prognostic significance is not definitely established. The fact, however, that this concn. is high in younger subjects in which, in general, the prognosis is poor, suggests that some relationship may exist. H. G.

Observations on the sugar of the blood and the sugar in the urine in varying conditions of health in the Bengali. II. D. MCCAY, *et al. Indian J. Med. Res.* **6**, 485–507(1919); *Endocrinology* **4**, 298; cf. *C. A.* **10**, 2763.—A general discussion of the relationship of the sugar of the blood to that of the urine and the factors concerned in regulating the excretion of sugar is entered into. The method employed was to det. the reducing power of the blood and urine by a special method in normal individuals, in glucosurics with normal kidneys and in individuals with nephritis. It was found that the threshold stimulus of the kidney for sugar excretion varies widely in different individuals and in the same person under different circumstances. Glucosurics are met with in cases where: (1) the threshold is high—usually the condition seen in the fat, over-fed classes; (2) the threshold is low—as in (*a*) the later stages of the above; (*b*) those who have lost the power of storing sugar, oxidizing it or of converting it into fat; (*c*) those who present an excessive permeability of the kidney to sugar as a result of oxaluria, gout, or stone. The limits of the normal variations of the sugar of the urine of Bengalis are from 0.015 to 0.15%, the av. being 0.065%. No parallelism or arithmetic proportions exist between the concn. of the sugar of the blood and that of the urine in any of the following conditions: (1) normal health; (2) aglucosuric diabetes; (3) varying degrees of glucosuria in different individuals; (4) varying degrees of glu-

cosuria in the same individual. The ingestion of glucose is always followed by an increase in the sugar of the urine, whether the sugar concn. of the blood increases or not, *i. e.*, in the healthy, potential diabetics, and diabetics. Kidney disease may prevent glucosuria even when very marked hyperglucemia is present—up to 0.86%. III. *Indian J. Med. Res.* 6, 508–49(1919); *Endocrinology* 4, 299.—The studies consisted of observations on the onset and progress of glucosuria with reference to the cause of the prevalence of diabetes in India. A large number of the natives from the various classes were examd. The authors believe that they have established the following points: (1) The fat, flabby, indolent individual who is over-fed with carbohydrates possesses a lower tolerance for carbohydrates than the lean, energetic, hard-working individual. (2) In the preglucosuric stage of diabetes, the fat and sugar of the blood are much above normal and are both increased still more by the ingestion of sugar. (3) As the ability of the tissues to convert sugar into fat is gradually diminished, sugar begins to appear in the urine and is found to increase as the fat content of the blood decreases. (4) A tendency to glucosuria occurs in normal persons when excessive amts. of sugar are ingested over long periods, hence the difference in the normal and the diabetic individuals is not a qual. but a quant. one. (5) The obesity so common in the preglucosuric or early glucosuric is associated with the hyperglucemia and is due to a physiological storing-up of reserve material, the excess sugar of the blood being synthesized into fat. (6) The subsequent wasting is probably pathological and may be explained as due to loss of the power of the tissues to convert sugar into fat and the actual breaking down of fat to furnish energy to the body. (7) There is a strong hereditary factor in diabetes. (8) The over-feeding with carbohydrates is said to be sufficient in itself to account for the onset of hyperglucemia, lipemia, obesity and glucosuria. (9) Excessive carbohydrate also is thought to lessen the secretion of the HCl of the gastric juice, which leads to gastrointestinal inflammation. This inflammatory process is said to spread in turn to the pancreas, causing a depression in the internal secretion, which condition interferes with the oxidation of sugar. H. G.

Experimental studies on tetany. E. FARNER AND R. KLINGER. *Mitt. Grenzg. Med. Chir.* 32, 469–97(1920); *Endocrinology* 5, 375–6.—In the cat nearly always small accessory parathyroids can be found in the thymus itself or its surrounding connective tissue. The authors removed in 40 cats the 4 principal parathyroids. The effect was not the same in all animals. Often an acute or sub-acute tetany developed which frequently ended fatally, but many animals remained in good health after the operation. This is probably not due to the remaining accessory glands as there was no correspondence between the existence of such glands and the symptoms. When sol. Ca salts are given these have a good influence on the symptoms. Twice the authors tried transplantation of a parathyroid to cure the postoperative tetany. In both cases temporary improvement was seen. Administration of thyroid had no or at most an unfavorable effect. Noël Paton has shown that guanidine or methylguanidine, when given to animals, produces symptoms closely resembling tetany. The authors consider tetany as an intoxication with guanidine compds. The function of the parathyroid would be to destroy (probably to oxidize) these substances. The good result following Ca treatment would be due to the fact that Ca salts give a ppt. with guanidine compds. The intensity of tetany would depend upon the quantity of parathyroid tissue and the quantity of guanidine compds. in the body. H. G.

The blood calcium content in normal children and in tetany. I. B. DE VRIES ROBLES. *Nederl. Tijdschr. Geneesk.* 63, (I), 1663(1919).—The author detd. by Wright's method the content of Ca in the blood of normal children and of children with tetany. He found no difference. He cannot confirm the results of other Dutch and German authors who found the amt. of Ca in tetany diminished. H. G.

Acetone in cerebrospinal fluid. J. KOOPMAN. *Nederl. Tijdschr. Geneesk.* **64**, 1346–50(1920); *Endocrinology* **4**, 450.—Acetone may be found in the cerebrospinal fluid in several pathol. conditions. During diabetic coma acetone and diacetic acid are found and the pressure is high. When the pressure in diabetes tends to rise it is often significant of approaching coma. Acetone and diacetic acid may be found in the cerebrospinal fluid in diabetic acidosis, also. In a case of adrenal apoplexy it was likewise found. H. G.

The saliva in diabetics. L. N. BOSTON AND L. W. KOHN. *N. Y. Med. J.* **105**, 497–502(1917); *Endocrinology* **3**, 554–5.—In diabetes the diastatic activity of the saliva varies within wide limits. In some cases the enzymic power was slightly higher than in normal cases. No definite relationship could be established between the diastatic energy of the saliva and the quantity of sugar in the urine. The saliva is more often acid than neutral or alk. Normal specimens of saliva have about the same degree of acidity, ranging from 0.0146 to 0.0219%. Excepting one case which was alk. in reaction, all the others (12 cases) exhibited acidities ranging from 0.00365 up to 0.07665%. Therefore, quite a number showed acidities higher than 0.03% when diastatic activity is supposed to be altered, and yet the diastatic activity sustained itself quite well. H. G.

Adrenal changes in experimental scurvy. Y. MORIKAWA. *Osaka Igakkwai* **19**, 9(1920); *Endocrinology* **4**, 615.—M. has found the following changes in the suprarenals in exptl. Barlow's disease in guinea pigs: (1) Increase in wt.; (2) increase in lipoidal content of the cortex; (3) reduction in amt. of doubly refractile fat; (4) distribution of the lipoid in the zona fasiculata in 3 layers—an outer rich in lipoid, a middle poor in lipoid and an inner rich in lipoid. He concludes that this hypertrophy, which is similar to that found in polyneuritis gallinarum, indicates that the absence of a necessary vitamine is also an etiological factor in Barlow's disease. H. G.

Humoral symptoms of Basedow's disease. L. SICILIANO *Riv. crit. clin. med.* (Firenze) **21**, 307–11(1920); *Endocrinology* **5**, 398.—S. reviews the several modifications of the blood (leucopenia and lymphocytosis and mononucleosis), the histological modifications of the thyroid, the variation in I content, the increase of adrenine, the glucosuria and hyperglucemia, the basal metabolism and Abderhalden's complement deviation, and finally the action of I on the thyroid function. All these researches are of help in the diagnosis of Basedow's disease, yet none of them is final, as a positive reaction can also be obtained in forms of pure hyperthyroidism (not yet pathological), so that to eliminate every doubt one has to go back to the study of the clinical symptoms and to the study of the course of the disease. H. G.

Acetone bodies in the blood in diabetes. R. FITZ. *Trans. Assoc. Am. Physicians* (Phila.) **32**, 154–8(1917); *Endocrinology* **3**, 354.—By the Van Slyke method the total acetone bodies, acetone, diacetic acid and β-hydroxybutyric acid were detd. and expressed as acetone. The degree of acidosis was detd. by measuring the combining power of plasma for CO_2. A series of 100 cases was tabulated, giving simultaneous detn. of total acetone in the blood plasma and degree of acidosis. Some of the cases had severe acidosis and others were acid free. No comatose cases or those having had alkali were included. No definite quant. relationship was discovered between increased concn. of acetone and lowering of blood bicarbonate, but in a general way the acetone rose as bicarbonate fell. The total acetone was increased by large amts. of fat, the max. occurring several hours after ingestion and after visible lipemia had disappeared. Small amts. of fat depressed blood acetone. Fasting and pure carbohydrate diet diminished high acetone. $NaHCO_3$ increased acetone output, but its effect on blood acetone was uncertain. In three fatal cases of coma it was observed that a rapid premortal rise of blood acetone occurred. In one case this was independent of acidosis. H. G.

Adrenaline content of the suprarenals in different diseases and a microchemical

reaction for adrenaline. S. OHNO. *Verhandl. jap. path. Ges.* (Tokio) **6**, 15(1916); *Endocrinology* **5**, 99.—Ohno finds Ogata's Ag method as satisfactory as the chrome reaction for detg. the adrenine content of suprarenal substance. He investigated the adrenine content of the glands in the case of various diseases. The av. amt. of adrenine in the left suprarenal of man was 2.82 mg. Among all the diseases studied, the patients having beriberi had the greatest quantity of adrenine. In 5 cases this averaged 9.45 mg. The least amt. was found in bronchial asthma. The quantity was fairly high in "contracted kidney," in 4 cases averaging 4.16 mg. The av. in hemophilia (number of cases not stated) was 9.16 mg. H. G.

Secretion of iodine in saliva in health and disease after subcutaneous injection of sodium iodide. E. ZAK. *Wiener. klin. Wochschr.* **33**, 281(1920); *Endocrinology* **4**, 452.—When NaI is injected subcutaneously it reappears in the saliva on the av. in 9 mins. and 40 secs., in men; in women after 7 mins. and 42 secs.; in men with osteomalacia in 5 mins. and 14 secs.; in women with the same disease it appears in 4 mins. and 54 secs. In osteomalacia the amt. of I excreted in the saliva is larger than normal. In diabetes insipidus, without treatment, it appears in about 4½ mins. Treatment with strychnine lengthened the period to about 10 min. H. G.

The blood sugar in narcosis and diseases of the nervous system. H. CHANTRAINE. *Zentr. inn. Med.* **41**, 521–9(1920); *Endocrinology* **5**, 99–100.—During ether narcosis the blood sugar is increased. This increase may range from 30 to 50%. During narcosis with EtCl the blood sugar remains unaltered. When C. experimentally produced concussion of the brain in rabbits by striking the heads with a hammer, no influence on the blood sugar could be detected. In patients with nervous diseases the quantity of blood sugar was the same as in normal persons. H. G.

Influence of free fatty acids in the intestinal contents on the excretion of calcium and phosphorus. S. V. TELFER. Univ. of Glasgow. *Biochem. J.* **15**, 347–54(1921).—The mode of excretion of Ca and P under conditions in which bile was completely or even partially absent from the intestine was studied. The subjects consisted of 2 cases of congenital biliary atresia, with complete exclusion of bile from the intestine, and one of jaundice in an infant suffering from syphilitic hepatitis, with partial exclusion of the bile. These 3 cases were compared with those obtained in the examn. of a normal infant. The subjects were placed on a "metabolism" bed, devized by Findlay, so that the urine and feces could be collected separately and quantitatively. The feces were dried on a steam-bath till const. in wt., then finely ground. Each daily quantity of urine was measured, acidified with HNO_3, and dild. to 1 l. The diet in all cases consisted of fresh cow milk contg. about 3% of fat. The Ca and P were detd. in the ash by the usual gravimetric methods. The neutral fat and free fatty acids were extd. directly from the feces with ether. The combined fatty acids were obtained by splitting the soaps with HCl, and extg. the fatty acids in a separating funnel. In complete exclusion of bile from the duct, over 70% of the dried feces may consist of fatty derivs. The Ca is found in the feces as soap in large excess of the normal, and the P, which is normally excreted by the bowel as $Ca_3(PO_4)_2$, is liberated from combination with Ca and is absorbed and eliminated by the urine. BENJAMIN HARROW

Significance of albumin and of albumin with casts in the urine. LOUIS I. DUBLIN. *Am. J. Hyg.* **1**, 301–10(1921).—The amt. of albumin was stated in terms of the Ogden scale. In a group of 2073 persons whose urine was found to contain *albumin only* (no casts) on several examns. in amts. exceeding the slightest possible trace, the total mortality was not far from double that for the best grade of insured persons even during the relatively short period (3 to 13 years) which followed their original examn. Cases in the age period 15 to 24 years showed no extra mortality when only a faint trace of albumin (slightest possible trace or very slight trace on the Ogden scale) was present; but

cases in this age period showed more than a double mortality when a trace of albumin (slight trace or trace on the Ogden scale) was present. "Apparently, it is not an impairment for young people 15 to 24 years old to have a faint trace of albumin even persistently; when the amt. of albumin rises to a trace, it appears to be a serious matter." Between the ages of 25 and 44 years, no marked difference existed between the 2 classes of albuminuria, although the mortality was very excessive in both—from slightly less than twice to more than 2.5 times that expected. After the age of 45 years, a faint trace of albumin apparently was less serious than a trace. The excess mortality in these cases was due primarily to Bright's disease, tuberculosis, and organic heart disease. In another group which included 3264 persons, *both albumin and casts* were present in the urine. At an av. period of over 6.5 years after the urinary examn., the actual mortality in this group was much higher than that expected; this held true for every age period, but was most striking for the period 14 to 24 years, in which the actual death rate was 2.5 times that observed in people of that age when only albumin was present. "This high death rate, however, applies only to those young people who show more than a faint trace of albumin with casts. There can be no doubt of the severity of the impairment of a trace or more of albumin with casts at these younger ages however doubtful may be the significance of a faint trace of albumin among very young people." The max. excess mortality lay in the age period 35 to 44 years. The excess mortality increased with the amt. of albumin. In conclusion, stress is placed on "the highly serious character of such impairments as albumin and albumin with casts. The gravity of the impairment varies directly with the amt. of albumin and not quite so regularly with the advancing age of the applicant. The presence of casts adds materially to the gravity of the impairment and granular casts add more to the defects than do hyaline casts. At the older ages, the presence of casts, together with albumin, is indicative of a condition of the greatest seriousness. At the younger ages, the presence of a trace or more of albumin or of albumin with casts suggests the existence of tuberculosis in many cases."

JOSEPH S. HEPBURN

Hemato-respiratory functions. XII. Respiration and blood alkali during carbon monoxide asphyxia. HOWARD W. HAGGARD AND YANDELL HENDERSON. Yale Univ. *J. Biol. Chem.* **47**, 421–32(1921); cf. *C. A.* **15**, 552.—CO asphyxia induces, not acidosis, but alkalosis. The lowering of blood alkali is due to the acapnial, not the acidotic, process in which various influences and conditions excite the respiratory center through agencies other than increase of C_H. This results in overbreathing (up to 300% or more) and an excessive elimination of CO_2 which leaves the blood abnormally alk. A gradual compensatory disappearance of alkali from the blood follows. The rate of O consumption is scarcely, if at all, decreased until death is imminent, but the respiratory quotient may be more than doubled. After section of the vagi, on the contrary, anoxemia due to CO causes no overbreathing, and no distinct lowering of the blood alkali, even up to death. This fact appears to be a decisive demonstration that O deficiency itself does not directly cause in the tissues and blood an increased production of org. acids.

A. P. LOTHROP

Enteral therapy of surgical tuberculosis with amino acids derived from animal tissues. R. HAFF. *Med. Klin.* **17**, 752–4(1921).—Assuming that a disturbed metabolism was associated with a localization of the tuberculous process a therapy consisting of the administration *per os* of amino acids from animal tissues was instituted. The amino acids were derived from articular tissues, blood and blood-forming tissues, and connective tissue. The most favorable and rapid results are reported in treatment of glandular tuberculosis; bone and joint infections were more refractory. G. H. S.

H—PHARMACOLOGY

ALFRED N. RICHARDS

Natural immunity of the rabbit to atropine. H. C. VAN DER HEYDE. *Arch. Néerland. physiol.* **5**, 380–433(1921).—Expts. on the rabbit, cat, and dog show that atropine is first bound physically by the serum proteins; this renders the atropine physiol. inert. The press juice from the organs of the rabbit destroys atropine more readily than do those of the cat. This explains the natural immunity of the rabbit to atropine. This immunity seems to be due to a substance formed by the leucocytes. The atropine-protein precipitant used was Mayer's reagent. H. V. ATKINSON

Prediction of physiological action of alcohols. O. KAMM. *Science* **54**, 55(1921).—In testing the toxicity of various normal primary alcs. to Paramecia, it was found to progress according to a simple numerical ratio on going up the series. MeOH exhibited an abnormality, but beginning with EtOH and expressing its action as unity, the acute toxicity of successive members when expressed in mols. increases according to a geometric progression. In a homologous series if the toxicity of any member is taken as unity, the subsequent members may be arranged as to toxicity according to the progression, 3, 3^2, 3^3, 3^4, 3^5, etc. In other words the toxicity of any member is 3 times that of the preceding one. The value of this lies in the fact that the rule may be extended to mammals and that, given the toxicity of any member of a series, the toxicity of any other member may be predicted. Examples are given. J. A. BRADLEY

Experimental toxicology. Part II. Organic substances. A. alkaloids. JOHANNES BIBERFELD. *Ergebnisse Physiol.* **17**, 1–362(1919); *Botan. Abstracts* **7**, 62. H. G.

The effect of painting the pancreas with adrenaline upon hyperglucemia and glucosuria. I. S. KLEINER AND S. J. MELTZER. *J. Exptl. Med.* **29**, 647(1919).—A difference exists in the effects on blood pressure and sugar production, depending upon the mode of administration of adrenaline. With regard to sugar production a subcutaneous injection has a definitely greater effect than an intravenous injection; with regard to blood pressure, however, the opposite is true. Herter had claimed that intraperitoneal injection of adrenaline gave a higher degree of glucosuria than subcutaneous or intravenous injection, and that the difference was due to the direct effect of the drug upon the pancreas. Kleiner and Meltzer tested this hypothesis and found that painting the pancreas, so isolated that no adrenaline could reach the peritoneum, gave a glucosuria about one-third, and a rise in blood pressure about two-thirds, that obtained by painting the un-isolated pancreas. Two facts were deduced: (1) that the painting of the isolated pancreas produces only mild glucosuria and hyperglucemia; and (2) that the greater production of sugar observed after painting the un-isolated pancreas cannot be of pancreatic origin. The authors are unwilling, however, to state whether the production of sugar is due to the escape of the adrenaline to some definite organ covered by the peritoneum (celiac ganglion or adrenals), or whether the peritoneum as a whole is responsible. H. G.

Increase of agglutinins after organotherapy as a proof of the stimulating action of organ preparations. L. BORCHARDT. *Therap. Halbmonatsh.* **34**, 536–41(1920); *Endocrinology* **5**, 253.—B. has previously reported that when anti-typhoid inoculations are accompanied by injections of adrenaline or hypophysin the agglutin titer is increased. In this article a similar increase is reported to follow the injection of spermine and of "asthymolysine." Thyroid administered by mouth has a similar influence. H. G.

Adsorption of poisons by constituents of the animal body. II. Adsorbent power of rabbit serum for atropine. W. STORM VAN LEEUWEN AND J. ZEYDNER. Leyden Univ. *Proc. Acad. Sci. Amsterdam* **23**, 486–505(1921); cf. *C. A.* **15**, 1939.—The

expts. were made to explain the relatively non-toxic action of atropine for the rabbit. While it may be due to all of the following, (*a*) insensitiveness to the poison, (*b*) chem. destruction of it, (*c*) poison rendered inactive, the last hypothesis is apparently proved. An adsorptive substance is assumed to be present in the serum. It is thermolabile, removed by filtration, can be frozen, thawed and dried. The action seems to follow the same laws as the adsorption of dyes by animal charcoal. H. C. HAMILTON

A quantitative inquiry into the antagonism pilocarpine-atropine on the surviving catgut. W. STORM VAN LEEUWEN AND C. VAN DEN BROEKE. Utrecht. Univ. *Proc. Acad. Sci. Amsterdam* **23**, 628–36(1921).—The authors describe and demonstrate the reliability of a biologic method for the assay of solns. contg. atropine. This depends on the relaxing action of the atropine on intestinal strips which had been contracted by the action of pilocarpine. The specimen is suspended in a vessel contg. Tyrode soln. to which is added pilocarpine soln. in varying quantities followed by sufficient atropine to counteract the contraction. Washing with fresh Tyrode removes the alkaloids and permits repeated expts. on the same specimen. The degree of activity of both alkaloids is directly proportional to the concns. of the solns. H. C. HAMILTON

Studies on neuromuscular transmission. I. The action of novocaine on muscle nuclei. J. F. FULTON, JR. Zoöl. Lab., Harvard. *Am. J. Physiol.* **57**, 153–70(1921).—Novocaine can be diazotized and combined with m-$C_6H_4(NH_2)_2$ to form a sol. dye "novocaine brown" $(NH_2)_2C_6H_3N{:}NC_6H_4COOCH_2CH_2N(C_2H_5)_2HCl$ having the physiol. properties of novocaine itself. The dye may be used histologically as a prepd. stain or it may be diazotized directly into the tissue (living or fixed) by dipping the tissue successively into novocaine, HNO_2, and m-$C_6H_4(NH_2)_2$, washing after each treatment. Novocaine brown stains only the nuclei of cells. Since novocaine and novocaine brown act in a way similar to curare, *i. e.*, on the receptive substance of the muscle and since novocaine brown appears to have an especial affinity for the nuclei of cells, it is suggested that the receptive substance of the muscle resides within the nuclei of the muscle fibers. J. F. LYMAN

Blast furnace gas poisoning (JOHANNSEN) 9.

I—ZOÖLOGY

R. A. GORTNER

Influence of thyroid extract and of other organ extracts on the metamorphosis and reproduction of Cyclops viridis and Cyclops serrulatus. ANITA VECCHI. *Arch. fisiol.* **17**, 105–36(1920); *Endocrinology* **5**, 400.—V. shows as a result of a large number of expts. on the crustacean, *Cyclops*, that feeding with various (mammalian?) organ exts. leads (1) to a marked abbreviation in the duration of the larval period, and (2) to a shortening of the time interval between the successive depositions of eggs by the female. These effects are exercized in the greatest degree by the ext. of thyroid, then by that of thymus, and to a less extent by those of the suprarenal and spleen. Ovarian ext. produces no well defined effects upon development—and may be compared in its action with the effect produced by a non-glandular substance such as fibrin. The duration of larval life in *Cyclops viridis* is about 28 days (20 to 34). Specimens allowed to hatch and undergo development in a thyroid medium metamorphose after 7 to 14 days; in thymus, after 11 to 17 days; in suprarenal and in spleen after 12 to 19 days. The expts. in which thyroid alone was fed in water were supplemented by expts. in which additional nutriment was supplied in the form of hay infusion contg. the protozoan, *Glaucoma*. But the accelerative effect of the thyroid was still very apparent, although the period of development was thereby shortened both in expts. and in controls. *Cyclops viridis* completes 5 depositions of ova in water in a 39-day period, in a thyroid medium in 28 days. Those grown in thymus require 29 days, the controls (in water) 34 days;

those in suprarenal 29 days, controls 34 days; those in spleen 30 days, controls 35 days. Negative results as regards development were obtained by the use of $FeCl_3$ in low concns. (Cf., however, positive results of Urbinati on *Cyclops macrunes*, 1913; Bios, **1**, 191–275.) V. concludes from the results of his expts. with *Cyclops* that the effects observed are probably due to specific organ hormones which normally promote metabolism, since they appear to exercize their effects in diverse degrees—certain ones giving marked positive results, others being indifferent. H. G.

Haploid and diploid parthenogenesis. PAULA HERTWIG. *Biol. Zentr.* **40**, 145–74 (1920); *Botan. Abstracts* **6**, 248.—Summary of known facts concerning maturation and development in artificial and physiol. parthenogenesis. Stimuli to artificial parthenogenesis are classed as chem., physical and biological. H. G.

The cytoplasmic inclusions of the germ cells. VI. The origin and probable constitution of the germ-cell determinant of Apanteles glomeratus, with a note on the secondary nuclei. J. BRONTÉ GATENBY. *Quart. J. Microsc. Sci.* **64**, 133–53(1920); *Botan. Abstracts* **5**, 50.—G. describes his attempts to det. the compn. and origin of the germ-cell determinant in the oöcytes of the parasitic hymenopteran, *Apanteles glomeratus*. He finds that it arises as a concd. area at the posterior pole of the young oöcytes; that it is probably formed of albuminous material rather than of chromatin, fat, yolk, or glycogen; and that the secondary nuclei have no connection with it. H. G.

The action of neutral isotonic salt solutions in sensitizing Arbacia eggs to the activating influence of hypertonic sea water. R. S. LILLIE AND MARGARET L. BASKERVILLE. Marine Biol. Lab., Woods Hole and Nela Research Lab., Cleveland. *Am. J. Physiol.* **57**, 110–24(1921).—Treatment of unfertilized *Arbacia* eggs with pure isotonic solns. of NaCl activates the eggs, without external signs of change, so that subsequent treatment (20 to 45 min.) to hypertonic sea water results in the production of swimming blastulae in many cases (as high as 50%). Other Na salts, $NaNO_3$, Na_2SO_4 and Na citrate, have a similar effect. The sensitizing effect of NaCl may be decreased although not prevented by the addition of $CaCl_2$ to the NaCl soln. Apparently it results from any sufficient change in the salt balance. Even pure isotonic $CaCl_2$ soln. produces the effect. The sensitized eggs show no visible changes; they do not form fertilization membranes and they may remain living and fertilizable for 24 hrs. or more. The sensitized condition is not appreciably reversed in sea water, but may persist for as long as 48 hrs.

J. F. LYMAN

The survival of motility in mammalian spermatozoa. C. G. L. WOLF. School of Agr., Cambridge. *J. Physiol.* **55**, 246–8(1921).—Rabbit spermatozoa may be kept motile for as long as 9 days by placing the juice of the epididymis in Tyrode soln. which has been buffered and to which an equal vol. of 0.125 mol. soln. of dextrose has been added. The soln. is adjusted to p_H 7.4, and oxygenated; then a suitable amt. of $NaHCO_3$ is added and the mixture kept at 1° and 2°. J. F. LYMAN

Studies on the respiration of insects. I. The gases and respiratory proteins of insect blood. RICHARD A. MUTTKOWSKI. Univ. Idaho. *Ann. Entomological Soc. Am.* **14**, 150–6(1921).—According to present knowledge, respiration among tracheates proceeds directly, that is, atm. O_2 is carried directly to the cells by means of tracheae, while the blood serves primarily for the transportation of food and metabolic products. This investigation was undertaken to det. whether the blood may function in the transportation of gases. Qual. tests with pyrogallol showed that the blood of all the species studied contained O_2; it also reacted to the oxidation tests for hemoglobin, although only Chironomid blood showed a positive hemin test. CO_2 was also present. Insect blood was found to contain Cu in amts. comparable to that found in crayfish blood where it forms the nucleus of the respiratory pigment, hemocyanin. The inference is that the Cu of insect blood also has a respiratory function. The sources of

the Cu were water, soil and food plants. The Malpighian tubules of insects do not function as an outlet for CO_2. "The role of insect blood is, therefore, in addition to its recognized function of circulating food and metabolic products, to aid the tracheal system in the distribution of O_2 to the tissues and to remove the CO_2." C. H. R.

A simple case of salt antagonism in starfish eggs. RALPH S. LILLIE. Marine Biol. Lab., Wood's Hole, and Nela Research Lab., Cleveland, O. *J. Gen. Physiol.* **3**, 783–94(1921).—The egg of the starfish, *Asterias forbesi*, is surrounded by a jelly-like substance, insol. in normal sea water but readily swelling and dissolving in pure isotonic NaCl soln. A small amt. of $CaCl_2$ added to the NaCl soln. entirely prevents soln. of the jelly, the jelly behaving in the mixed soln. exactly as in normal sea water. The action of $CaCl_2$ in preventing soln. of the jelly is parallelled with its action in preventing the agglutinating, cytolytic, membrane formation, and maturation effects of pure NaCl soln. on the living egg. It is inferred that the essential factor in these and other similar antagonistic and protective actions is the formation of water-insol. colloidal salts (soaps and proteinates) of Ca or other metals with the structural colloids of the protoplasm. The presence of a certain proportion of such compds. is apparently necessary to the structural stability of protoplasm, especially to the water-insoly. and semipermeability of its external layer. When the cell is immersed in NaCl soln., water-sol. Na compds. are substitited for the insol. Ca compds. normally present and disintegration of the cell results. CHAS. H. RICHARDSON

12—FOODS

W. D. BIGELOW AND A. E. STEVENSON

Albert Frederick Seeker. R. E. DOOLITTLE AND P. B. DUNBAR. *J. Assoc. Official Agr. Chem.* **4**, 602–4(1921).—An obituary. E. J. C.

Industrial waste of food products. G. A. MENGE. *Chem. Met. Eng.* **25**, 435–6 (1921). E. J. C.

Technically trained men, the need of the food-preservation industries. W. V. CRUESS. *Chem. Met. Eng.* **25**, 435(1921). E. J. C.

Vitamines of dried milk. WILH. STEPP. *Med. Klin.* **17**, 287–8(1921).—Highly active accessory food substances are present in dried milk powders. G. H. S.

A modified Babcock method for determining fat in butter. M. W. HEPBURN. Cornell Agr. Expt. Sta., *Mem.* **37**, 669–90(1920).—Nine g. of butter are used in an 18 g. 40% cream bottle, and 9 cc. of warm H_2O added and followed by adding 17.5 cc. of H_2SO_4. After mixing the water, fat and acid, sufficient H_2O is added to bring the vol. to the base of the neck in the bottle. It is centrifuged for 9 min. Samples are removed, set in a water bath and temperatured at from 125° to 130° F. "Glymol" is added to remove the meniscus. The reading is multiplied by 2 to get % of fat in the butter. The method gives results which correspond closely with those obtained by chem. analysis. J. J. SKINNER

Drying and preserving of egg preparations. L. BRIANT AND H. W. HARMAN. *Nat. Assoc. Rev.* **38**, 247–51(1921).—The baking value of eggs lies in their power of retaining gas produced by baking powders, etc., in the dough, and the value is dependent on the amt. of coagulable albumin present. In the case of dried eggs a portion of the albumin may be coagulated during the drying process, especially if the temp. exceeds 65° F. (19° C.), and the loss due to coagulation is increased by the presence of small quantities of boric acid. J. S. C. I.

Meat-packing industry contributes too much to fertilizer. L. M. TOLMAN. *Chem. Met. Eng.* **25**, 437(1921). E. J. C.

Substitutes for sucrose in curing meats. RALPH HOAGLAND. Bur. Animal Ind. U. S. Dept. Agr., *Bull.* **928**, 1–28(1921).—Results of expts. in curing pork hams and

sweet-pickle bacon indicate that such sugar substitutes as dextrose, cerelose, 70% corn sugar and refiners' sirup can be used successfully in place of cane sugar in curing this class of meats. In curing expts. with beef hams the use of dextrose and cerelose yielded dried beef of as good quality as that obtained by the use of cane sugar, but beef hams cured with 70% corn sugar and with refiners' sirup were of inferior quality. The expts. with box-cured bacon yielded conflicting results, some of the tests indicating that there was little difference in the quality of the bacon cured with dextrose and cerelose as compared with that cured with cane sugar, while other tests indicated that bacon cured with cane sugar was of distinctly superior quality. W. H. Ross

Our cereals as a source of fats and the significance of the aleurone layer to the seed. P. LINDNER. *Jahresber. Ver. angew. Botan.* **16**, 29–31(1918); *Botan. Abstracts* **7**, 230–1.—There is 9 times as much fat in the aleurone layer as in the germ; consequently about a million tons of fat from the grain harvest go into the bran each year. This was formerly fed to cattle but during the war was used in bread. Although cattle digest this fat, it passes unchanged through the human alimentary tract. If, however, the cell walls of the aleurone layer are first dissolved by acid, the fat becomes digestible for man. This fat is deposited in the aleurone layer and hulls of the grain to prevent water from penetrating to the interior. H. G.

Calcium hydrogen phosphate. T. UMBACH. *Pharm. Ztg.* **66**, 565(1921).—A critical discussion of Loeffl's article (cf. *C. A.* **14**, 3481). **Reply.** LOEFFL. *Ibid* 599. W. O. E.

Vanilla and vanillin. ANON. *Chem.-Ztg.* **45**, 696–8(1921).—A presentation, historical and descriptive, of the vanilla industry and the importance and shortcomings of synthetic vanillin in this connection. There is included the method for detg. vanillin in vanilla essence recommended by W. M. Doherty (*C. A.* **8**, 2580). C. C. Davis

The research chemist in the fruit-products industry. H. A. NOYES. *Chem. Age* (N. Y.) **29**, 385–6(1921). E. J. C.

A study of the factors affecting temperature changes in the container during the canning of fruits and vegetables. C. A. MAGOON AND C. W. CULPEPPER. Bur. Plant Ind. U. S. Dept. Agr., *Bull.* **956**, 1–55(1921).—The rate of change of temp. in the can is influenced by the fineness of the material, its compn. and the amt. and viscosity of the free liquid. NaCl and dil. sugar solns. have very little effect on the rate of change of temp., but concd. sugar solns. and solns. of starch have a very marked retarding effect on the rate of change of temp. at the center of the can. In 5% starch the consistency becomes such that all convection is stopped and the rate of change is very slow. Increasing the percentage of starch further has very little effect upon the temp. changes. In a can packed with material having an interspace filled with a free liquid, as in string beans, the rate of change of temp. at the center of the can is very rapid and with such materials the glass container has a marked effect on the rate of rise of temp., but in materials of a heavy or pasty nature, as in sweet corn, the rate is very slow unless mechanical agitation is employed and the effect of the glass container is then of little importance. W. H. Ross

The prickly pear (Opuntia). Possibilities of its utilization. CHAS. F. JURITZ. *S. African J. Ind.* **3**, 687–93, 803–14(1920); *Botan. Abstracts* **7**, 94.—The possibility is discussed of utilizing the prickly pear as a useful fodder plant for stock and as an article of human diet. It is also considered as a source of potash fertilizer, of sugar and vinegar, of industrial alc., of oxalic acid, of oil, of a mucilaginous glaze, of sizing for textile fabrics, of fiber for paper making, of a dye or coloring matter, and as a basis for soap manuf. From a practical standpoint not more than 7 or 8 of these seem to be deserving of serious attention. H. G.

Oil cakes. F. J. PLYMEN. Dept. of Agr., Central Provinces, India. *Bull.*

No. 6, 10 pp.(1919).—This is a discussion of oil cakes as a cattle food and fertilizer. The point is made that from the standpoint of digestibility all oil cake for stock food should be ground. E. SCHERUBEL

Removing the bitter principle and utilizing lupines. GERLACH. *Mitt. deut. Landw. Ges.* **35**, 619–20(1920); *Botan. Abstracts* **7**, 229.—G. reviews some of the methods used to remove the bitter principle from lupine seed. He points out that the high cost of protein in Germany at this time may warrant the expense involved in utilizing the large amts. of protein in lupine seed for cattle feed and even as human food. H. G.

The use of woody materials for feeding cattle. II. Investigations on wheat straw. F. SCURTI AND G. DROGOUL. *Staz. sper. agrar. ital.* **52**, 490–6(1919); cf. *C. A.* **14**, 3732. Wheat straw analyzes 2.53% fat, 3.64% crude protein, 33.76% cellulose, 4.90% ash, 55.17% non-nitrogenous ext. and 27.30% pentosans. The ground straw was treated with NaOH soln., 25% H_2SO_4, HCl, and 25% HNO_3 similarly to the treatment of corn cobs. The straw consists of lignified cellulose analogous to that of the corn cobs which is only partially split up by NaOH under pressure. Treatment with alkali gives only traces of sugars. Hydrolysis with acids under pressure seps. the straw into cellulose and reducing sugars. When 10% of 25% H_2SO_4 is used, 60% cellulose and 32% sugars are produced at 130° in 2 hrs. ALBERT R. MERZ

Five-hundred tons of fresh forage per hectare by means of the elephant grass of Rhodesia. MARIO CALVINO. *Rev. agr. com. y trabajo* **3**, 172–83(1920); *Botan. Abstracts* **7**, 228.—The Napier or elephant grass (*Pennisetum purpureum* Schum.) was introduced into Cuba by C. in 1918. Analyses showing the food value and the mineral constituents are given. The water content of the fresh grass is 24.5–38.2%. H. G.

Sweet silage as feed for milk cows. M. POPP AND R. FLOSS. *Mitt. deut. Landw. Ges.* **35**, 391–4(1920); *Botan. Abstracts* **7**, 97.—The authors describe an expt. with a form of ensilage, the making of which is said to have been developed in Switzerland. The process is not described in detail, but reference is made to previous papers. In the expts. reported rowen was used from a grass meadow. One portion of the rowen was made into hay, and the other put into a silo under pressure. The feeding expt. was carried on for varying periods, hay and the sweet silage from the same rowen grass being used. Analyses showed that the fat content and the crude protein content were the same for both hay and silage. The pure protein and the digestible protein were, however, greater in the hay; while the amides increased in the silage. The cows gave more milk from the silage than from the hay; and even after the supply of silage was exhausted, the cows that had been fed on it appeared to retain the increased milk flow. The making of sweet silage is highly recommended. H. G.

Wood preparation for fodder. P. WAENTIG. *Naturw. Z. Forst- u. Landw.* **17**, 44–53(1919); *Botan. Abstracts* **3**, 303.—Various theories as to the usefulness and availability of the food stored in wood are described; the fact is taken into consideration that stem- and branch-wood, on account of greater lignification, may have much less food value than leaves and twigs, which are eaten naturally by stock and have long been cured for fodder. Various means for making the nutrients available are described, of which the most successful process seems to be a combined mechanical and chem. treatment. Grinding or cutting, as in the prepn. of paper pulp, is of no avail because of the incomplete opening of the cells and the loss of nutrients through the watering which must accompany so intensive a mechanical process. As fodder, wood seems to be especially deficient in proteins, and must be supplemented by some rich food such as animal meal. Its similarity to straw, in this and other respects, is repeatedly mentioned. In spite of its deficiencies, it may be recommended, especially for work-animals, as the rougher part of the ration. H. G.

The purification basins at Strassburg and the breeding of Cyprinides (JOLYET) **14.** Deastringency in the fruit of *Diospyros kaki* (TOKUGAWA) **11D.** Preparation of palm oil for edible purposes (ANON.) **27.** Purifying fatty glycerides (U. S. pat. 1,381,564) **27.**

Cereal food. J. D. BOURDEAU and W. B. FINK. U. S. 1,381,858, June 14. Cereals such as oats which are apt to become rancid are treated with sufficient soln. of $Ca(OH)_2$, NaOH or other alk. substance to combine with the free acid of the cereal oily constituents and also to form a loose combination with the carbohydate components which serves to neutralize any subsequently liberated free acid.

Cereal food. C. ELLIS. U. S. 1,382,963, June 28. A human food is formed by soaking bran in fruit pulp contg. sugar in soln. and then drying the bran at a temp. high enough to produce curling of the flakes.

Edible fat and oil mixture. J. H. JONES. U. S. 1,381,468, June 14. A congealed churned edible mixt. is formed of sweet cream or oleomargarine ingredients flavored with an edible lactic bacilli culture. U. S. 1,381,469 relates to a method of prepg. a mixt. of the same character.

Preserving coconut or other similar food products. V. A. WHITE. U. S. 1,382,038, June 21. Food particles, *e. g.*, coconut, are first coated with glycerol and then with a powdery substance such as flour which prevents adhesion of the particles.

Dry coffee mixture. J. GREENBERG. U. S. 1,381,821, June 14. A dry mixt. suitable for prepg. a beverage with H_2O is formed of dry coffee ext. and dry milk having a fat content greatly reduced as compared with unmodified dry milk. U. S. 1,381,822 relates to a similar prepn. in which a coffee substitute ext. is used instead of coffee ext.

Grape-juice sirup. S. AVIS. U. S. 1,381,613, June 14. Whiting is thoroughly mixed with grape juice and then allowed to settle and the juice is decanted from the settled material and concd. to a sirup. This neutralizes or removes the active ferment of the juice so that it will remain sweet for an indefinite time.

Soluble albumin from whey. A. C. WEIMER. U. S. 1,381,605, June 14. The acid content of whey is neutralized and the whey is then concd. at a temp. below the pptg. temp. of albumin to such a degree as to cause crystn. of most of the lactose. The latter is sepd. and the whey is dialyzed to remove salts and additional lactose and the H_2O is finally removed at a temp. below the pptg. point of albumin to produce a product contg. the albumin, a small amt. of lactose and some of the salts of the milk. Th s product is suitable for use in *baking*.

13—GENERAL INDUSTRIAL CHEMISTRY

HARLAN S. MINER

The past year in industrial chemicals. GUY A. GARDNER. *Chem. Age* (N. Y.) **29,** 346(1921).—A market review. E. J. C.

Preliminary summaries of 1919 census of manufactures. ANON. *Chem. Met. Eng.* **25,** 465–70(1921).—Statistics for chemicals, drug prepns., natural dyes and exts., fertilizers, gas, leather, paper and wood pulp, pretroleum refining, rubber goods, soap, brass, bronze and Cu products, pig Fe, industrial power and fuel consumption in superpower zone. E. J. C.

Our foreign trade in chemicals. O. P. HOPKINS. *J. Ind. Eng. Chem.* **13,** 753–6 (1921); cf. *C. A.* **14,** 2972. E. J. C.

Works accounts from the chemist's point of view. RAYMOND CURTIS. *J. Soc. Chem. Ind.* **40,** 175–6T(1921).—About costs. E. J. C.

Chemical research for the industries of India. E. R. WATSON. *Chem. Age* (London) **5,** 234–7(1921).—An address. E. J. C.

Economic importance of waste products utilization. WALTER H. DICKERSON. *Chem. Age* (N. Y.) 29, 339–42(1921). E. J. C.

Human waste in industry. HARRY E. MOCK. *Chem. Met. Eng.* **25**, 369–74(1921). **Waste due to poor engineering and management.** DEXTER S. KIMBALL. *Ibid* 375–7. **The educational waste in industry.** HOLLIS GODFREY. *Ibid* 378; cf. *C. A.* **15**, 403. **The role of research in waste elimination.** HARRISON E. HOWE. *Ibid* 379–82. **Waste due to lack of standardization of chemicals.** WALLACE P. COHOE. *Ibid* 383–4. **The personal problem: To eliminate the waste of human effort.** L. B. HOPKINS. *Ibid* 385–8. **Disclosing waste through better cost methods.** ERNEST J. WESSEN. *Ibid* 389–93. **The elimination of construction wastes.** GEO. W. BURPEE. *Ibid* 394–6. **Some considerations on fire waste.** NICHOLAS RICHARDSON. *Ibid* 397–400. **Location as a factor in eliminating industrial waste.** VICTOR V. KELSEY. *Ibid* 401–2. **Reduction of waste through accident prevention.** L. A. DEBLOIS. *Ibid* 403–6. **Elimination of waste in industry due to poor lighting.** WARD HARRISON. *Ibid* 407–9. **Eliminating manufacturing wastes with machinery.** J. E. HIRES. *Ibid* 410–2. **Elimination of waste in industrial power plants.** DAVID MOFFATT MYERS. *Ibid* 413–6. **The elimination of waste in marketing.** WM. R. BASSET. *Ibid* 420–2. **Wastes in litigation.** WELLINGTON GUSTIN. *Ibid* 423–7. **Eliminating waste and nuisance in smoke, fume and gas.** P. E. LANDOLT. *Ibid* 428–32. **The wastes caused by carelessness.** PHILIP DEWOLF. *Ibid* 433.—In addition to the papers noted here this special number of *Chem. Met. Eng.* contains a number of brief articles on wastes in specific industries which are referred to separately in the appropriate sections of this number of *C. A.* E. J. C.

Importance of knowledge of production costs to efficiency in chemical manufacture. RAYMOND CURTIS. *Chem. Age* (N. Y.) **29**, 366–7(1921). E. J. C.

Relation of university chemical departments to chemical industry. BENJAMIN F. LOVELACE. *Chem. Age* (N. Y.) **29**, 357–9(1921). E. J. C.

The patent situation [in the U. S.]. EDWIN J. PRINDLE. *Chem. Met. Eng.* **25**, 417–9(1921). E. J. C.

The British patent system. J. HAROLD BEAUMONT. *Perf. Essential Oil Record* **11**, 223–4, 255–7, 312–5, 400–1; **12**, 293–5(1921). E. J. C.

Waterwheel test by chemical means. R. C. STARR. *Elec. World* **78**, 509(1921).—One of the difficult problems to be dealt with in tests of hydroelec. units in place is the accurate detn. of the discharge through the wheels. The chem. method of measuring the power delivered to the wheel is simple and comparatively accurate. The method consists of introducing at a const. rate a known concd. soln. of NaCl into the penstock, then taking samples of water at the tailrace and titrating with 0.02 *N* $AgNO_3$ soln. to det. the NaCl concn. The amt. of diln. of the original soln. dets. the quantity of water passing through the wheel. The cu. ft. per sec. is equal to: ratio of diln. $\times 62.4 \times d/w$, where 62.4 is the wt. in lbs. of a cu. ft. of water, d the sp. gr. of the concd. NaCl soln. introduced into the penstock and w the wt. of this soln. introduced per sec. Full details are given. G. G. F.

Power from mercury vapor. W. L. R. EMMET. *Elec. World* **78**, 517(1921).—Brief report of recent tests on the use of Hg in place of H_2O in boilers. Of the 1050 kw. delivered by the Hg boiler tested about 850 kw. constituted net gain as compared with a 200-lb. steam process operating with similar firing conditions. C. G. F.

Extraction apparatus and extraction practice (Voss) **1.**

Recovering vapors of volatile liquids. G. A. BURRELL, C. L. VORESS and V. C. CANTER. U. S. 1,382,889, June 28. In recovering vapors of volatile liquids such as gasoline, C_6H_6, alc., CCl_4, NH_3 or CH_2O, gas mixts. contg. relatively large amts. of

recoverable vapors are dild. with gas contg. a small amt. of vapors, in order to dissipate excess heat from the recovery app.

Recovering vapors from gaseous mixtures. G. A. BURRELL, C. L. VORESS and V. C. CANTER. U. S. 1,382,890, June 28. Vapors of volatile liquids such as gasoline, C_6H_6, alc., ether, acetone, $CHCl_3$, CCl_4, or NH_3 or CH_2O are taken up by an absorbent, *e. g.*, activated charcoal or silica gel, and are then distd. with steam under pressure and condensed.

Factory air-clarifiers and fume collectors. A. NASHLUND. Can. 212,428, July 12, 1921. An app. for recovering fumes from retorts or stills consists of a casing surrounding the retort or still, means for circulating air through the casing and means for agitating the air within the casing.

Conduit of fibrous and waterproofing material. R. P. PERRY. U. S. 1,382,740, June 28. Hollow cylinders adapted for use as conduits are formed of a mixt. of fibrous pulp and pitch, asphalt or resin densified to a rigid condition by heat and pressure.

Absorbent for use in ice machines. C. M. SMITH and H. WEIGAND. U. S. 1,383,247, June 28. An absorbent for use in ice machines is formed of anhydrous $CaCl_2$ with charcoal distributed throughout the mass.

14—WATER, SEWAGE AND SANITATION

EDWARD BARTOW

The purification basins at Strassburg and the breeding of Cyprinides. A. JOLYET. *Rev. eaux forêts* **58**, 195–202(1920); *Bolan. Abstracts* **7**, 117.—The problem of sewage disposal has been solved at Strassburg by the construction of stagnant ponds in which the org. material is assimilated by protozoans, worms, crustaceans, insect larvae, molluscs, etc., and these in turn are eaten by carp and other fish. The latter are entirely safe for human consumption and have no disagreeable taste. One hectare of pond is sufficient to dispose of the sewage from 2000 to 3000 people (nearly ten times as many as can be cared for by filtering the waste water in settling basins), and at the same time to support an abundant population of fish. This method suggests to foresters the possibility of introducing org. matter into the many ponds and streams found in the plains where communal forests cover more than 20% of the land area, and of using these for the breeding of carp and other Cyprinides, which would form an important addition to the *food supply* of the country. H. G.

Influence of peptone on indole formation by *B. coli* (TILLEY) **11C**. Report of the Imperial Agricultural Bacteriologist (HUTCHINSON) **15**. Determining the finer dust particles in air (MEYER) **7**. Corrosion of iron and its prevention by the elimination of the gases dissolved in water (PARIS) **9**. Apparatus for electrically heating and sterilizing water (U. S. pats. 1,382,156, 7-8-9) **1**.

Base-exchanging silicates. H. J. WHEATON. U. S. 1,381,777, June 14. A soln. of Na silicate is partially neutralized with HCl and the resulting gelatinous mass is dried and washed to free it from any excess of sol. salts and to render it suitable for use as a water purifying and softening material.

15—SOILS, FERTILIZERS AND AGRICULTURAL POISONS

J. J. SKINNER AND ALBERT R. MERZ

How the fertilizer industry can prevent wastes. CHARLES H. MACDOWELL. *Chem. Met. Eng.* **25**, 445–6(1921). E. J. C.

The determination of borax in fertilizer materials and mixed fertilizers. G. F.

LIPSCOMB, C. F. INMAN AND J. S. WATKINS. *J. Assoc. Official Agr. Chem.* **4**, 599–601 (1921).—See *C. A.* **14**, 2234. E. J. C.

The utilization of ammoniacal gas waters as fertilizer. Preliminary note. CORRADO BONGIOVANNI. *Staz. sper. agrar. ital.* **52**, 521–3(1919).—The liquid is added to acid phosphate until effervescence which is due to evolution of CO_2 ceases. $Ca(NH_4HPO_4)_2$ and $Ca((NH_4)_2PO_4)_2$ are formed and HCN is expelled by decompn. of the cyanides. Excess H_2O is evapd. and drying completed in a ventilated room at moderate temp. The fertilizer is ashy in color, practically odorless, non-hydroscopic and keeps well under normal conditions. It contains no cyanides or thiocyanates. Material manufd. from 15% acid phosphate contained 12.48% H_2O, 12.58% H_2O- and citrate sol. P_2O_5 and 3% N. ALBERT R. MERZ

Fertilizing with carbon dioxide. GERLACH. *Mitt. deut. landw. Ges.* **35**, 370–1 (1920); *Botan. Abstracts* **6**, 129.—The expts. on the effect of increasing the CO_2 content of the air, first reported in 1919, were repeated in a light, airy greenhouse. In a small section of the house the air was made to contain 23 times as much CO_2 as it had before the expt. No beneficial results were obtained. H. G.

Some soil studies. W. P. HEADDEN. *Proc. Soc. Promotion Agr. Sci.* **39**, 22–38 (1919); *Botan. Abstracts* **6**, 204; cf. *C. A.* **13**, 1734.—The accumulation of excess amts. of nitric N in the soil is given as the cause of low yields and poor quality in both the sugar beet and wheat crops of Colorado. An increase of 40 pts. per million of nitric N in the surface foot of soil depressed the sugar content of beets from 15.4 to 11.9% and produced other unfavorable results. It was found that a certain soil which had a max. of 20.5 pts. per million on March 4 showed a steady increase of nitric N during the summer. On August 25 the minimum was 47 pts. per million and the max. 333 pts. per million of nitric N. H. believes that certain Colorado soils have the power to fix atm. N by converting it into protein N through the agency of their bacterial flora, the *Azotobacter*. In expts. with soil taken from the fields he found a max. N fixation of 124 pts. per million in 48 days. This rate of fixation would add 1.5 tons of protein matter to the acre foot of soil in 48 days. H. G.

Report of the Imperial Agricultural Bacteriologist. C. M. HUTCHINSON. *Sci. Rept. Agr. Res. Inst. Pusa* **1918–19**, 106–14(1919); *Botan. Abstracts* **5**, 298.—The report summarizes investigations on nitrification, N fixation, green manuring, biol. analyses of soils, indigo manuf., pebrine disease of the silkworm, and sterilization of water. H. G.

Report of the Imperial Agricultural Chemist. W. H. HARRISON. *Sci. Rept. Agr. Res. Inst. Pusa* **1918–19**, 35–45; *Botan. Abstracts* **5**, 296.—From studies in the method of *retention of superphosphate in soil*, it is concluded that the phosphate is held in non-calcareous soils by absorption, and in calcareous soils by chem. combination, and therefore the range of application and method of employment of superphosphate as fertilizer must be different in the two types of soil. *Sugar cane* (*Saccharum officinarum*) stored in windrows in the North-West Frontier Province shows increasing content of both glucose and sucrose, but other changes render the final sucrose yield nearly const. with continued storage. Immediately following heavy rainfall there is rapid deterioration of the cane. In *fertilizer expts. with rice* (*Oryza sativa*), green manure combined with $(NH_4)_2SO_4$ gave an increase in yield almost exactly proportional to that given by sulfate alone. H. G.

The fixation of nitrogen in Colorado soils. WM. P. HEADDEN. Colorado Agr. Expt. Sta., *Bull.* No. **258**, 48 pp.(1921).—Nitrates occur abundantly in the surface soil of certain sections of Colorado. The waters of shallow wells and the surface soils are closely related in regard to nitric N. The waters of deep wells are free from nitric N. The ground waters derive their NO_3 from the soil and the amt. is detd. by local conditions. The surface soil, especially at the edge of these niter areas, has a very

high capacity for fixing N. Nitrates occurring in these areas have no source outside of the area and on the surface. RUSSELL M. JONES

The formation of soluble substances in soils taken from widely separated regions. M. M. McCOOL AND C. E. MILLAR. *Soil Sci.* **10**, 219–35(1920); cf. *C. A.* **14**, 2231, 2525.—The rate of formation of sol. substances in surface and subsoils from widely sepd. areas of the U. S. was detd. by the f.-p. method. So-called new soils are less active than those somewhat older and the aged soils are almost inert. Subsoils form sol. salts very slowly. The finer separates of a soil are chiefly responsible for the formation of sol. salts in the samples of soils investigated. Grinding the separates increases their soly. When the separates were treated with 0.1 *N* $NaNO_3$ and washed free of sol. material the rate of formation of sol. substances was increased. W. J. R.

Orchard cover crops. JOSEPH OSKAMP. Indiana (Purdue) Agr. Expt. Sta., *Bull.* No. **248**, 42 pp.(1920).—The most satisfactory orchard cover crop is the one which, in the locality under consideration, will produce the greatest growth of vegetation relatively rich in N. Rye, vetch, millet, and buckwheat crops rank high in the amt. of dry matter and N returned in their crop residues, while soy beans, clover and weeds rank low. RUSSELL M. JONES

Natural reproduction in the pine heaths of Norrland. II. HENRIK HESSELMANN. *Skogsvårdsfören. Tid.* **17**, 29–76(1919); *Botan. Abstracts* **3**, 296; cf. *C. A.* **14**, 2044.—Lichen-covered soils in which pine seedlings grow poorly are low in nitrates. The presence of decaying wood or leaves mixed with the mineral soil promotes nitrification. Mixing sod with the soil, or even merely stirring it with a hoe causes marked improvement. T. G. PHILLIPS

Chemical requirements of peat soils in the light of European experience. F. J. ALWAY. *J. Am. Peat Soc.* **13**, 327–41(1920); *Botan. Abstracts* **7**, 72.—European peat soils are placed in two classes: those with (1) low lime requirements, and (2) high lime requirement. H. G.

Pyrites and its toxic oxidation products in peat soils. C. O. ROST. *J. Am. Peat Soc.* **13**, 303–6(1920); *Botan. Abstracts* **7**, 72.—Fe sulfide is widely distributed in peat soils. It appears mostly as pyrite, which is insol. in water. In air it is oxidized to $FeSO_4$ and H_2SO_4, both of which are sol. and toxic to plants. H. G.

Bees and their relation to arsenical sprays at blossoming time. W. A. PRICE. Indiana (Purdue) Agr. Expt. Sta., *Bull.* No. **247**, 15 pp.(1921).—For the sake of the bee fruit trees should not be sprayed while in full bloom. A sufficient amt. of poison is found in lead arsenate or other arsenical sprays applied to the blossoms to cause a tremendous death rate of bees. A very small amt. of As (less than 0.0000005 g. As_2O_3) is a fatal dose for a bee. The Gutzeit method of detg. As appears to be positive enough for a dose that is injurious to bees. RUSSELL M. JONES

Anticryptogamic product. R. LANCE. *Compt. rend.* **172**, 1201–2(1921).—The material recommended is prepd. by dissolving 1 kg. of $ZnSO_4$ in 100 l. of water, adding 500 g. of lime to ppt. the Zn as hydroxide, and then 80–100 g. of an ultramarine color. Finally 250 g. of $Al_2(SO_4)_3$ are added and the whole is well shaken and after filtering is ready for use. This mixt., it is claimed, combines the antiseptic action of Zn with the microbicidal action of the blue, violet, and ultra-violet rays. J. S. C. I.

Oil cakes (PLYMEN) **12**. The carbon dioxide assimilation of cultivated plants (VORNEMANN) **11D**. The prickly pear. Possibilities of its utilization (JURITZ) **12**. Determination of arsenic in arsenates (BELL) **7**.

Insecticide. J. D. NEULS. U. S. 1,381,586, June 14. An insecticide for fumigating trees is formed of HCN and mustard oil or other material which has an irritating and stimulating effect on insects.

16—THE FERMENTATION INDUSTRIES

H. S. PAINE

Alcohol—The important part it plays in the industries of the world—Its position in Canada. P. A. HILL. *Can. Chem. Met.* 5, 233(1921). E. J. C.

Influence of degree of ripeness of fruit [for wine making] on the acceleration of fermentation by various nitrogenous compounds. Cellar experiments to obtain pure fermentation and stability of fruit wines. Lactic acid malady appearing in fruit wines after complete fermentation of the sugar. Importance of blending for the stability of mild fruit wines. H. MÜLLER-THURGAU AND A. OSTERWALD. *Landw. Jahrb. Schweiz* 1920. J. S. C. I.

The role of acetaldehyde in alcoholic fermentation. A. FERNBACH AND M. SCHOEN. *Bull. inst. Pasteur* 18, 385–406(1920); *Botan. Abstracts* 7, 311–2.—A review and a synthetic study of our knowledge on the subject. The work of Neubauer and Fromhertz on the breakdown of the amino acids in the animal body by the path of analine α-aminopropionic acid—pyruvic acid—acetaldehyde—ethyl alc. is taken as a starting point for the review. The work of Neuberg and Karczag, Neuberg and associates, Fernbach and Schoen, Mazé and Lintner and Liebig, J. B. Dumas, Connstein, and Leudeke has shown that the above reactions can be brought about by yeast juice and are due to a special enzyme which has been named carboxylase, since it has the power of forming CO_2 from the carboxylic group. This same enzyme has been found active in various organisms, among which are various forms of *Oidium* and several bacterial species. The work of Neuberg and Reinfurth showed the role of sulfites in the production of AcH by the yeast cell, and the work of Neuberg and Kreb led to the assumption that methylglyoxal was formed as one of the steps in the action, a substance which could easily yield glycerol. Thus the classical formula of fermentation would take the form of $C_6H_{12}O_6$ = AcH + CO_2 + $C_3H_5(OH)_3$, and in presence of sulfites the action would be symbolized by $C_6H_{12}O_6 + Na_2SO_3 + H_2O = C_3H_5(OH)_3 + CH_3CH(OH)O.SO_2Na + NaHCO_3$. In 1919 Neuberg and Hirsch have shown that the living yeast, if allowed to act in an alk. medium in absence of sulfites, forms AcOH in large quantities. A direct oxidation of the aldehyde cannot be assumed, since the action is taking place in an atm. of CO_2; furthermore, the ratio of AcOH to glycerol is 1:3. Applying the Cannizzaro reaction to the oxidation of AcH and uniting it with the reaction of Neuberg and Reinfurth one has: $2AcH + H_2O = CH_3CH_2OH$ + AcOH and $2C_6H_{12}O_6 = 2C_3H_5(OH)_3 + 2CO_2 + 2AcH$. A list of the articles cited is appended. H. G.

Electrochemical methods for the investigation of the addition of sulfuric acid to wines. LUIGI CASALE. *Staz. sper. agrar. ital.* 52, 549–68(1919).—The increase of ash does not correspond to the quantity of H_2SO_4 added while the alkalinity of the ash diminishes much less than proportionally to the added acid. The ash remains alk. even when H_2SO_4 is added in amt. greater than the alkalinity of the ash. While the ash detd. by the electrochem. method corresponds in N and plastered wines to that obtained by weighing it is higher in wines to which H_2SO_4 has been added. The addition of H_2SO_4 causes the formation of both neutral and acid K sulfates, the presence of both salts being only shown by electrochem. methods which depend on cond. detns. with the Wheatstone bridge. ALBERT R. MERZ

Various fermentation tests with the addition of purified yeasts. A. CAUDA. *Staz. sper. agrar. ital.* 52, 524–35(1919).—Pure yeasts cause fermentation to start earlier and to proceed much more regularly. There is less decompd. sugar in the wine and less acidity because less alc. is consumed in secondary reactions. Fermentation develops very rapidly in musts to which N is added and is completed first in the liquid

with $(NH_4)_2CO_3$, second in that contg. asparagine, third in that with peptone. These compds. favor the formation of yeasts in the order named. Phosphatic salts also promote the growth of yeasts. Musts to which nitrogenous compds. have been added give colors tending toward yellow, a sign of rapid aging. The use of asparagine is advizable. ALBERT R. MERZ

The relation between the principal acids of wine. E. GARINO-CANINA. *Staz. sper. agrar. ital.* **52**, 536–41(1919).—The values of the ratios (1) total tartaric acid × 100 : total determinable acidity + alkalinity of the ash and (2) total lactic acid × 100: total determinable acidity + alkalinity of the ash and (3) total malic acid × 100: total determinable acidity + alkalinity of the ash are shown for numerous wines in tables or by graph. For young wines (3) ranges around 41%. This is diminished to half or more in old wines. For young wines (2) averages 10% and it leaps to 28–30% in old wines. The values of the ratios vary with the source, with the vintage, and with other factors. The value of (1) reaches 70% for some Tuscan wines while some wines of Avellina have a value as low as 7%. Piedmont, Emiliana and Sicilian wines vary from 15% to 45%. There are no noteworthy differences met with in white wines.

A. R. M.

Determination of extract yield from raw grain (maize and rice). W. WINDISCH AND P. KOHLBACH. *Woch. Brau.* **38**, 57–9, 63–4, 76–7(1921).—A comparative study of various methods. In the one recommended 40 g. of the maize or rice is mixed with 150 cc. of water and 100 cc. of a filtered malt ext. (made by digesting 1 pt. of malt with 4 pts. of water for 1 hr. at 30° with frequent stirring). Next morning the mash is heated rapidly to 70°, then in 40 mins. to 80°, and then boiled for 5 mins. on a sand-bath. After cooling to 50° it is treated with a further 100 c.c. of malt ext. and the temp. is maintained at 50° for ½ hr., raised to 70° in 20 mins., maintained at 70° for 25 mins., raised to 75° in 5 mins., and maintained at 75° for 30 mins. The cooled mash is made up to 450 g. before filtering. The method of calcn. is explained fully.

J. S. C. I.

Comparative experiments respecting the most convenient method of calculation and the accuracy attainable in the pycnometric determination of extract in malt analysis. H. KEIL. *Woch. Brau.* **38**, 95–6(1921).—In accurate detns. of wort gravities by the pycnometer, tedious corrections for air displacement under different conditions of barometric pressure may be avoided by the use of a "compensation pycnometer" (*i. e.*, a counterpoise such as a pycnometer suitably loaded with shot and hermetically sealed, having approx. the same wt. and vol. as the pycnometers in use when the latter are filled with water). The exact wt. of the counterpoise is detd. once for all, and the extra wts. required in one pan or the other to balance a pycnometer filled with water or wort against the counterpoise are added to or subtracted from the wt. of the latter. J. S. C. I.

The prickly pear. Possibilities of its utilization (JURITZ) **12.** Fusel oil tester (NOLL) **1.** Detection of methanol in liquors and spirits (HOTON) **7.**

Preserved malt preparation. B. A. HOEHL. U. S. 1,381,833, June 14. A stable mixt. adapted for prepg. a malt extract is formed of hops, malt and malt sirup.

17—PHARMACEUTICAL CHEMISTRY

W. O. EMERY

Synthetic drugs in America. E. H. VOLWILER. *Am. J. Clin. Med.* **28**, 365–8 (1921).—An outline of some of the more important synthetic medicinal chemicals manufd. and used in the U. S. E. J. C.

Glycerol and its many uses. ANON. *Chem. Age* (London) **5**, 237(1921).—A description is included of the principal *substitutes* (15 in number) introduced in Germany.
E. J. C.

The differentiation of cocaine hydrochloride, novocaine and stovaine, and their identification in binary mixtures. G. BATTA AND C. GENOT. *J. pharm. Belg.* **3**, 449–457(1921).—The adulteration of cocaine-HCl is practiced very extensively at the present time as a result of the recent enactment of laws to prevent its use by habitués. The adulterants most frequently met with are novocaine and stovaine. These cannot be distinguished from cocaine-HCl by their appearance or by organoleptic tests; their solubilities in different solvents (see table *D* in orig. article) are very much alike; and they behave similarly toward the following reagents: NaOH soln., $HgCl_2$ soln., Lugol's soln., $AgNO_3$ soln., and HgCl with EtOH. They can be distinguished most easily by the following means: (1) The m. p. of cocaine-HCl is 156°, that of stovaine 183°. (2) Five drops of $KMnO_4$ soln. (1:1000) are decolorized immediately by 5 cc. of a 1:50 soln. of novocaine to which have been added 5 drops of dil. H_2SO_4. The $KMnO_4$ soln. is decolorized slowly by cocaine-HCl under similar conditions. (3) Five cc. of cocaine-HCl soln. (1:50) to which have been added 5 drops of $FeCl_3$ soln. (1:10) and 5 drops of recently prepd. $K_3Fe(CN)_6$ soln. (1:20) becomes green in color immediately and finally yields a blue ppt. Cocaine-HCl produces no change in the $K_3Fe(CN)_6$ soln. (4) On heating 0.1 g. of cocaine-HCl with 1 cc. of concd. H_2SO_4 at about 100° for 5 min. and then pouring the liquor into 2 cc. of H_2O, the odor of BzOMe becomes perceptible. On cooling, crystals of BzOH are deposited. Novocaine does not give the odor nor the crystals by this treatment. (5) Dissolve 0.1 g. of novocaine in 5 cc. of H_2O and add 5 drops of dil. HCl and 2 drops of $NaNO_2$ soln. (1:10). To this soln. add 0.2 g. of β-naphthol dissolved in 1 cc. of NaOH soln. A copious scarlet-red ppt. will form. If this ppt. is added to concd. H_2SO_4, a violet-red soln. will result. Neither stovaine nor cocaine-HCl gives this reaction. (6) If 3 to 4 cc. of Cl water and 3 to 4 drops of $PdCl_2$ soln. are added to a few drops of cocaine-HCl soln., a red ppt. will form. Under similar conditions, novocaine gives a dirty green color and stovaine produces no change in the reagents. (7) If 3 drops of fuming HNO_3 are added to 1 drop of an aq. soln. of novocaine, followed by several drops of a soln. consisting of 5% of resorcinol dissolved in 10% KOH soln., an intense red color will develop. Neither cocaine-HCl nor stovaine gives this reaction. (8) On adding a 10% soln. of $ZnCl_2$ to a 5% soln. of novocaine, a white ppt. will be produced. No ppt. forms in the case of cocaine-HCl or stovaine. (9) In neutral soln., K_2CrO_4 yields a ppt. with solns. of stovaine, but not with cocaine-HCl or novocaine. A yellow ppt. is produced in acid solns. of cocaine-HCl (See table *A* in orig. article for details). (10) A 5% soln. of $Na_2B_4O_7$ produces a white ppt. in solns. of cocaine-HCl and stovaine, but not in solns. of novocaine. (For details, see table *B* in orig. article.) (11) The test with NH_4OH soln. carried out according to the French Pharm. gives a cryst. ppt. on standing in the case of cocaine-HCl, the supernatant liquid remaining clear; novocaine solns. yield only a slight deposit after long shaking, the supernatant liquid remaining opalescent; stovaine solns. become milky immediately and do not become clear within ½ hr. (12) With Na_2HPO_4, solns. of stovaine become milky immediately, solns. of novocaine do not ppt. at all and solns. of cocaine-HCl become slightly opalescent only after long standing. To detect the adulteration of cocaine-HCl with stovaine, the β-naphthol or resorcinol reactions are the most satisfactory. By the former, 0.5% of novocaine can be detected and by the latter as little as 0.1%. To detect cocaine-HCl in novocaine, the reaction with H_2SO_4 or the $Na_2B_4O_7$ test gives the best results. The latter serves to detect cocaine-HCl in quantities as small as 10%.
A. G. DuMez

Matriculation sheets. A. SCHAMELHOUT. *J. pharm. Belg.* **3**, 459, 477, 493,

507, 508, 548, 565(1921).—Tentative monographs proposed for introduction into the Belgian Natl. Formulary are submitted for the following items: Cryst. ergotinine, iron tannate, emetine, iron cacodylate, $Fe(OH)_3$, ferric hypophosphite, ferrous oxalate, iron monomethylarsinate, $FeCl_2 + 2H_2O$, and $FeSO_4$ (dried). A. G. DuMez

American essential oils. G. A. Russell. *Am. Perfumer* **16,** 244–6(1921).—A brief review of the production of Am. essential oils. W. O. E.

Conception of medicaments in patent law and interpretation by the German patent office. F. Heinemann. *Z. angew. Chem.* **34,** Aufsatzteil, 361–3(1921).—An address embodying the conception of medicaments as defined by various authors, the attitude of the patent office with respect thereto, and suggestions for modifications in the law, in the interpretation of the office, or in both. W. O. E.

Manufacture of thymol from ajowan. J. V. Lakhani, J. J. Sudborough and H. E. Watson. *J. Indian Inst. Sci.* **4,** 59–84(1921).—Expts. have been carried out on the distn. of ajowan seed, using stills contg. 300 lbs. and 1500 lbs., resp., the yield of oil varying thereby from 2.5 to 3.5%. The quantity of steam required to distil 1 lb. of oil was about 100 lbs. for fresh seeds, but as much as 150 lbs. for old seeds. New methods are given for sepg. the thymol from the oil and for refining the former by distn. with superheated steam. The yield of pure thymol from the seed was about 1%. Summaries are given of the sources, syntheses and uses of thymol. Figures for the cost of thymol in India are appended. W. O. E.

Popular medicaments for dropsy, and their significance. F. Netolitsky. *Pharm. Monatshefte* **2,** 61–9(1921).—A discussion. W. O. E.

The study of Polygonum bistorta. Localization of tannin. Its employment as a substitute for Krameria triandra. N. Wattiez. *Ann. bull. soc. roy. sci. med. nat. Bruxelles* **4,** 121–8(1920); *Botan. Abstracts* **7,** 191.—In Belgium, during the war, the use of Cod liver oil being prohibited as a food and tonic, the iodo-tannic sirup was prescribed frequently. The want of rhatany necessitated the search for an indigenous substitute. This has been found in the rhizome of *Polygonum bistorta* which contains 15 to 18% of tannin. H. G.

Bay oil. J. Jones. *Rept. Agr. Dept., Dominica,* **1918–19:** 5. *Imp. Dept. Agr. Barbados* **1919;** *Botan. Abstracts* **5,** 109.—Two samples of oil from varieties of *Pimenta acris,* namely Bois d'Inde and Bois d'Inde Citronelle, grown in Dominica, are reported on. The latter variety contains a smaller percentage of phenols, and has a strong odor of citral, and the suggestion is made that it may have some com. value in the manuf. of toilet prepns. H. G.

Camphor. J. Jones. *Rept. Agr. Dept., Dominica* **1918–19:** 5–7; *Imp. Dept. Agr. Barbados.* **1919;** *Botan. Abstracts.* **5,** 109.—Results of distns. of leaves, twigs and prunings from 3 plots showed that 2 of them were of true camphor trees, yielding both camphor and oil, while the other was not, the material from it producing oil only. H. G.

Two remarkable organic identifications. James Moir. *J. S. African Assoc. Anal. Chem.* **4,** No. 2, 15–9(1921).—The steps taken to find out that the active constituent of the sneezing powder "cachoo" was *dianisidine* and that a druggist had dispensed *novatophan* in place of aspirin are described in interesting detail. W. T. H.

Essential oil of Boronia pinnata, Sm., and the presence of elemicin. H. G. Smith. *Proc. Roy. Soc. Victoria* **32,** 14–9(1919); *Physiol. Abstracts* **5,** 257.—An account is given of the chem. and physical consts. of elemicin, now for the first time extd. from *Boronia,* of the oil of which it forms 75%. E. H.

Mustard oil in plants. A. Cauda. *Staz. sper. agrar. ital.* **42,** 541–8(1919); cf. *C. A.* **14,** 3498.—The quantity of oil remains almost const. during germination of the seed but decreases greatly on etiolation of the seedling. Thus black mustard

seed contains 0.294%, air-dried green seedlings 0.280%, air-dried and etiolated seedlings only 0.170%. ALBERT R. MERZ

Heeria berries of South Africa as a source of oil. ANON. *Bull. Imp. Inst.* **19**, 24–5(1921).—Fruits of *Heeria paniculosa* were examd. as a source of oil. The pericarp yielded an amt. equal to 5.5% of the wt. of the entire fruits. The oil consists chiefly of terpenes, is mobile and colorless and possesses no characteristic odor. The consts. of this oil were: d_{15} 0.832, α_D + 3.75, acid value 1.6, ester value before acetylation 4.2 ester value after acetylation 14.8. The crushed fruits, after removal of the volatile oil by distn., furnished a quantity of fixed oil equiv. to a yield of 30% from the entire fruits. The oil was clear, dark brown and had an aromatic odor. R. L. SIBLEY

Determination of cresol (CHAPIN) **11B.** Vitamines and certain aspects of their relation to public health (DRUMMOND) **11E.** Bay trees (ROBSON) **11D.** Ajowan plant (ROBSON) **11D.** American horsemint (ROBSON) **11D** Manufacture of chloroform (OCHI) **10.**

Metal pyrophosphate casein compounds. A FREY. U. S. 1,381,295, June 14. Casein (without previous dissolving in alkali) is dissolved with a soln. of Na pyrophosphate and a metal salt such as $CaCl_2$ or $FeCl_3$ is added. Stable compds. are formed which are readily sol. in alk. solns. and are adapted for use as *therapeutic agents.*

Compounds of cinchona alkaloids and 2-phenyl-quinoline-4-carboxylic acid. A. B. DAVIS. U. S. reissue 15,127, June 21. See original patent No. 1,213,464, *C. A.* **11**, 1016.

Surgical sutures. C. T. DAVIS. U. S. 1,382,715, June 28. Surgical sutures are treated with coal-tar dyes to render them antiseptic and also to differentiate sutures of different character by different colors which are applied to them. Among the dyes which may be used are: "mercurochrome-220," "gentian violet," "crystal violet" and "brilliant green."

18—ACIDS, ALKALIES, SALTS AND SUNDRIES

FRED C. ZEISBERG

The physico-chemical aspects of sulfuric acid manufacture. A. O. JONES. *Chem. Trade J.* **69**, 183–5(1921).—Equil. and reaction velocity of the reaction $2SO_2 + O_2 \rightleftarrows 2SO_3$ are discussed and the work of Haber, Bodenstein and Knietsch on this reaction is reviewed. Nothing new is brought out. F. C. Z.

New method of purification of hydrochloric acid. J. LAMQUET. *Bull. soc. chim. Belg.* **29**, 309(1920).—Com. HCl may be freed from As, Cl, and SO_2 by the simple addition of H_3PO_2 or one of its salts, the reactions being represented by the following equations: (1) $3H_3PO_2 + 4AsCl_3 + 6H_2O = 3H_3PO_4 + 12HCl + 4As$. (2) $H_3PO_2 + 2Cl_2 + 2H_2O = H_3PO_4 + 4HCl$. (3) $H_3PO_2 + SO_2 = H_3PO_4 + S$. By using the Ba salt H_2SO_4 is pptd. at the same time. J. S. C. I.

The technical preparation of nitric acid from the air by means of gas explosions. F. HAUSSER. *Stahl u. Eisen* **48**, 956–62, 999–1003(1921).—When a mixt. of air and H or illuminating gas is exploded NO is formed. This reaction forms the basis for a simple method of prepg. HNO_3 from the air. The app. required is much simpler than for any other technical method of prepn. Assuming that the reaction is strictly due to the thermal effect of the explosion, the theoretical yield of NO can be calcd. from the temp. and concn. of the reacting gases by the following equations: $\log K + (9424/T) = 1.07$ and $K = (NO)^2/[(N - 0.5\,NO)(O - 0.5\,NO)]$. Expts. with a bomb of about 500 cc. capacity give results in good agreement with the theory but with larger bombs the results show 90–120% more than the theoretical yield. This is not accounted for by the greater

amt. of available O or the less heat radiation but is similar to the observation of Haber and König (*C. A.* **2**, 626) on NO formation in cooled high-tension arcs. Technical expts. were made using air and illuminating gas and using air, illuminating gas and O. A bomb holding 100 l. was used. The results without the addition of O showed 9–12 g. HNO_3 per cu. m. of the exhaust gas. With the addition of O the yield was increased to 18 g. HNO_3 per cu. m. The pressure used was 3–4 kg. per sq. cm. Shortly before the World War a plant was erected at a Westphalian coke plant for the trial of this process. The capacity is 7000 cu. m. gas daily, 300 l. bombs being used. The purified gas and air enter the bomb at 300° and under a pressure of 5.5–6 kg./cm.^{2} It was found that the yield is increased and the process simplified if some O is used with the mixt. The bombs make 44–45 explosions per min. The exhaust gases go into a kind of marine boiler where they are cooled to 250°. Up to this point iron has been used for all the app. From the boiler the gases go into Al coolers and are cooled to water temp. and then pass to absorption towers where a 27–28% HNO_3 is made. The gas which passes through the water absorption towers is absorbed by soda soln. to form $NaNO_2$. The nitrite liquor contains 24% $NaNO_2$, 0.7–0.8% $NaNO_3$ and some bicarbonate. The further development of the process seems to be along the lines of making larger bombs. The calcn. of the strength of the bomb is discussed in some detail in an appendix. R. S. DEAN

The nitrate question as it affects the future of the United States. COURTENEY DE KALB. *Mfrs. Record* **80**, No. 8, 69–71; No. 9, 97–100(1921). E. J. C.

Need of technically trained men in salt manufacture. W. L. BADGER. *Chem. Met. Eng.* **25**, 442–3(1921). E. J. C.

Chromite in 1920. EDWARD SAMPSON. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Pt. I, pp. 21–8(preprint No. 4, published Aug. 17,1921). E. J. C.

Magnesium in 1920. RALPH W. STONE U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Pt. I, pp. 17–20(preprint No. 3, published Aug. 18, 1921). E. J. C.

Fuller's earth in 1920. JEFFERSON MIDDLETON. U. S., Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 39–40(preprint No. 5, published Aug. 25, 1921). E. J. C.

Solution of bleaching powder. M. CHAMPION. *Bull. soc. chim. Belg.* **29**, 24–8 (1920).—Mixts. of bleaching powder and water contg. from 1 to 20% of the former were shaken for 3 hrs., allowed to settle, and in the clear supernatant soln. the active O, total Cl and Ca, and the d. were detd. If the concn. exceeds 4% there is a risk of some of the active O being retained in the residual sludge from the prepn. The figures on the whole show rather higher proportions of Ca and total Cl to active O than those required by the formula, ClCaOCl. J. S. C. I.

The nitrogen problem. J. A. WILKINSON. Univ. Coll., Johannesburg. *S. African J. Sci.* **17**, 95–110(1920).—A review of com. processes for the fixation of atm. N together with statistics on the consumption of N compds. in S. Africa. W. H. R.

Developments in nitrogen fixation. J. A. HARKER. *Electrician* **87**, 218(1921).—Present status of the N-fixation industry in Great Britain. Of the world's total production in 1920 of 671,300 tons of fixed N the Empire produced but 12,800 tons, all of which came from Canada. Germany produced 420,000 tons of fixed N from the air besides the 150,000 tons from by-product coke ovens. C. G. F.

The manufacture of pure hydrogen and the catalytic hydrogenation of oils (MAXTED) **27**. Electric oven for baking pencil leads (WEAVER) **1**. Acid pumps without stuffing boxes (FINKELSTEIN) **1**. Determination of sulfur in roasted pyrites (SIEBER) **7**.

Concentration of nitric acid. F. C. ZEISBERG. Can. 212,753, Aug. 2, 1921. A mixt. of HNO_3 and H_2SO_4 is subjected to a current of steam or hot gases, the HNO_3

vapors are removed and condensed, the uncondensed vapors are passed through an absorbing app. and the resulting HNO_3 is conveyed to the mixed acids being subjected to the current of steam. App. is specified.

Ammonia and ammonium compounds. G. G. and I. E. KNAPP, JR. Can. 180,816, Dec. 4, 1917. A N-contg. material, *e. g.*, "dimetal isocyanide," is treated with steam below 350° to the point of satn. and then the temp. is raised to or above 450° while the steam treatment continues.

Cyanogen compounds. J. C. CLANCY. Can. 186,179, Aug. 20, 1918. The product resulting from a synthetic reaction between C, N and Na_2CO_3 in the presence of Fe as a catalyst is cooled and treated with liquid NH_3, which dissolves out the cyanogen compd.; this compd. is recovered from soln. and the residue is used over again. The process is an improvement on the Bucher N-fixation process.

Fluorides. H. B. BISHOP. U. S. 1,382,165, June 21. A mixt. such as is obtained from Na_2SiF_6, H_2O and Na_2CO_3 is treated with NaOH to render the siliceous compd. sol. and the latter is sepd. from the fluoride. KF or MgF_2 or other fluorides may be similarly made from silicofluorides.

Sodium hypochlorite. J. R. MACMILLAN. U. S. 1,383,224, June 28. In the manuf. of NaOCl soln., Cl is led into a mixt. of lime and Na_2CO_3 soln. and the $CaCO_3$ formed is sepd. from the resulting NaOCl soln.

Iron salt ($FeSO_4Cl$). O. RÖHM. U. S. 1,383,264, June 28. An Fe salt of the formula $FeSO_4Cl$ is formed by treating $FeSO_4$ soln. with Cl and heating. It is suitable for use in *tanning*.

Potassium compounds from cement-kiln gases. H. V. WELCH. U. S. 1,382,037, June 21. Cement-kiln gases or the like are treated with H_2O in such a manner as to obtain a satd. soln., and the sludge thus obtained is then heated to render additional K compds. sol. and the soln. is sepd. from the residue for recovery or utilization of its values.

Separating borax from potassium salts. C. E. DOLBEAR. U. S. 1,382,825, June 28. Mixts. such as deposits from Searles Lake brine contg. K salts and borax are heated and centrifuged in moist condition and the resulting liquor, principally contg. borax, is sepd. from undissolved material.

Selenium oxychloride. V. LENHER. U. S. 1,382,920, June 28. Se oxychloride is formed by the interaction of SeO_2 and $SeCl_4$ in the presence of CCl_4 or other solvent.

Selenium oxychloride. V. LENHER. U. S. 1,382,921, June 28. Se oxychloride is formed by reaction of H_2O on $SeCl_4$ in the presence of CCl_4 or other solvent of the product.

Selenium oxychloride. V. LENHER. U. S. 1,382,922, June 28. Se oxychloride is produced by the interaction of SeO_2 and HCl followed by treatment of the products with $CaCl_2$ or equiv. dehydrating agent.

Phosphorus oxychloride. T. L. BARTLESON. U. S. 1,381,783, June 14. P oxychloride is formed by bringing phosgene into contact with molten metaphosphoric acid, at a temp. of 330–40°.

Purifying zinc solutions. S. FIELD. U. S. 1,382,494, June 21. Foreign metals are removed from Zn solns. (such as $ZnSO_4$ solns. from ores) by treating the soln. in slightly acid state with $HgSO_4$ and Zn powder at a temp. of 70–100°.

Recovery of nitrogen oxides. P. A. GUYE. Can. 212,391, July 5, 1921. Oxides of N are recovered from a mixt. of gases by oxidizing the oxides to produce a mixt. of oxides of N which will not solidify above 0° and then liquefying the oxides by refrigeration. Cf. *C. A.* **14**, 1196.

The recovery of nitrous oxides. P. A. GUYE. Can. 212,392, July 5, 1921. Nitrous oxides are recovered from a mixt. of gases by liquefying the oxides at a temp.

of at least −20° by direct contact with a refrigerating liquid capable of dissolving the oxides without interacting therewith.

Process for the fixation of nitrogen. F. L. SLOCUM. Can. 180,800, Dec. 4, 1917. Carbide is treated with N in the presence of a C halide, *e. g.*, CCl_4. A completely or partially nitrified material or a mixt. of both serves as a catalyst. **Cf. *C. A.* 14, 102.**

Agglomerating carbon or other materials. T. ROUSE. U. S. 1,381,748, June 14. Ferroborosilicate is used as a binder for graphite for furnace electrodes, etc., with steam and subsequent heat treatment to produce a firm product resistant to moisture.

Treating materials with gas or vapor. F. L. SLOCUM. Can. 180,798, Dec. 4, 1917. CaC_2 is treated with N. The nitrified material is subjected to the action of steam until the NH_3 formation is complete and then the temp. of the mass is raised to expel all the water and CO_2 from the residual material. The complete process is conducted in a continuous series of operations in the same app.

Waterproofing composition. T. BOSSHARD. U. S. 1,383,068, June 28. A waterproofing compn. adapted for use on *paper* or *cloth* is formed of gelatin 8 oz., H_2O 18 oz. and glycerol 9 oz.

Fireproofing solution. G. BLENIO. U. S. 1,382,618, June 28. A soln. for fireproofing wood or fabrics is formed of H_2SO_4 5 gals., H_3BO_3 crystals 15 lbs., H_3PO_4 10 gals., H_2O 100 gals. and sufficient NH_3 to neutralize the soln.

Polishing composition. H. SHACKLETON and J. GORDON. U. S. 1,382,127, June 21. A compn. adapted for polishing varnished surfaces or marble is formed of equal amts. of raw linseed oil, malt vinegar, turpentine and alc.

Polish for glass or metals. H. SWANSON. U. S. 1,381,250, June 14. A mixt. adapted for polishing Ag, Au or glass is formed of H_2O 8 oz., naphtha soap 1.75 oz., pptd. $CaCO_3$ 4 oz. $NaHCO_3$ 0.15 and cream of tartar 0.24 parts.

"Moisture-preventing composition." W. H. BRABANT. U. S. 1,381,788, June 14. A solid mixt. adapted for use on windshields to promote coalescence of H_2O globules is formed of sugar, paraffin and an aq. tobacco ext.

Heat insulating material. O. GERLACH. U. S. 1,381,118, June 14. An insulating material adapted for use in furnace walls is formed by mixing infusorial earth with H_2O to form a paste and then adding dil. sulfite liquor, $(NH_4)_2CO_3$ and HOAc.

Printing-plate matrix. H. M. BLAETZ. U. S. 1,382,713, June 28. A matrix for making printing plates is formed with a backing of ductile easily moldable metal such as Pb and a matrix face mechanically united with the backing and formed of an exceedingly thin film of a hard non-oxidizing metal such as Sn.

Abrasive. J. A. MENARD. U. S. 1,381,728, June 14. An abrasive convertible by rubbing into a lubricant, adapted for use in grinding and polishing machine parts, is formed of potash, $PbCO_3$ or $PbSO_4$, Na, and marble, limestone or onyx, with or without lampblack.

Valve-grinding abrasive mixture. J. V. WICKS. U. S. 1,381,953, June 21. A mixt. adapted for grinding valves is formed of a "petroleum hard oil," lard oil and a pulverized abrasive such as carborundum.

Stove polish. A. J. STENCELL. U. S. 1,382,026, June 21. A stove polish is formed of lubricating graphite 2 lbs., "stove polish" 2 lbs. and oil of sassafras 0.125 oz.

Combustion chambers for sulfur burners. F. B. CHAPPELL. Can. 212,691, July 26, 1921. The chamber has a baffle wall arranged out of normal to the inlet passage to the chamber so as to impart a swirling motion to the incoming stream of gas. The baffle wall has small openings affording communication between the inlet and outlet passages.

Ventilating sleeves for sulfur burners. F. B. CHAPPELL. Can. 212,692, July 26, 1921. A ventilating sleeve, which has a tubular body and inwardly projecting

tubular air conduits, is connected to the combustion chamber and spaced from the burner to provide an air admission space.

Feeding devices for sulfur burners. F. B. CHAPPELL. Can. 212,690, July 26, 1921. A feed spout for S burners is open at the discharge end and at the top adjacent to the discharge end.

19—GLASS, CLAY PRODUCTS, REFRACTORIES AND ENAMELED METALS

G. E. BARTON, C. H. KERR

Waste in the glass industry. E. WARD TILLOTSON, JR. *Chem. Met. Eng.* **25,** 437–8(1921). E. J. C.

The electrical properties of glass. J. R. CLARKE. *Beama* **8,** 235–8(1921).—A review including a bibliographical list of 38 references. C. makes a number of definite recommendations on the basis of his own experience and that of others. For glass line insulators, in addition to the elec. and mechanical properties, one has also to consider cost. This necessitates the manuf. from cheap materials, in a tank furnace, thus excluding the use of Pb. The surface leakage must be low and hence the resistance to chemical attack fairly high; the specific inductive capacity should be low, to reduce flashover and the dielec. strength fairly high to prevent penetration. The coeff. of expansion must be low and the glass should be well annealed. All these conditions indicate a glass of high SiO_2 content. A potash-lime glass with as high a SiO_2 content as possible would be best on the basis of present data. Further research is needed. For glass condensers, a Ba-borosilicate glass has so far proved to be most serviceable. C. G. F.

Progress of colloidal chemistry in ceramics since the end of the world war. H. ARNOLD. *Kolloid-Z.* **29,** 105–6(1921). E. J. C.

Production wastes in the ceramic industry. R. H. MINTON. *Chem. Met. Eng.* **25,** 440–1(1921). E. J. C.

Silica in 1919. L. M. BEACH. U. S. Geol. Survey, *Mineral Resources of U. S., 1919,* Part II, 379–80(preprint No. 28, published Aug. 27, 1921). E. J. C.

Electrical conductivity of glass (POOLE) **2.** Polish for glass (U. S. pat. 1,481,250) **18.**

Cleansing and polishing paste for glass. J. M. SCHWANER. U. S. 1,382,019, June 21. The mixt. is formed of whiting 58 lbs., powdered pumice 16 lbs., kerosene 19 lbs., Na_2CO_3 3 lbs., NaCl 3 lbs. and essential oils such as oils of citronella and geranium 2.5 oz. each.

Crucibles. W. A. DARRAH. U. S. 1,381,171, June 14. Crucibles are made by mixing fine and coarse ground coke and alumina with a colloidal binder such as fireclay and with sufficient H_2O to form a liquid mixt., pouring the mixt. into a mold of plaster of Paris or other porous material which will absorb fluid from the mixt., and finally baking, after removal of the mold.

20—CEMENT AND OTHER BUILDING MATERIALS

C. N. WILEY

Cement industry needs more chemical engineering. JOHN GODFREY DEAN. *Chem. Met. Eng.* **25,** 439–40(1921). E. J. C.

The preparation of slag for road ballast. I. Slag dressing at the Georgs-Marien Hütte at Osnabruck. HORST V. SCHWARZE. **II. Slag dressing at the Friedrich**

Alfred-Hütte in Rheinhausen. W. SCHÄFER. *Stahl u. Eisen* **41**, 919–23(1921).—The material is broken up and graded according to size; the material for road building is up to 25 cm. in diam. R. S. DEAN

Sand-lime brick. JEFFERSON MIDDLETON. U. S. Geol. Survey, *Mineral Resources of U. S., 1920*, Part II, 37–8(preprint No. 4, published Aug. 24, 1921). E. J. C.

Wood decay (SCHMITZ) **11A.** Potassium compounds from cement-kiln gases (U. S. pat. 1,382,037) **18.**

RUDOLF, SALIGER: **Der Eisenbeton, seine Berechnung und Gestaltung.** Stuttgart: Alfred Kröner. 522 pp. M 30. For review see *Stahl u. Eisen* **41**, 1207(1921).

Waterproofing cement. L. M. KREGELIUS. U. S. 1,382,986, June 28. A waterproofing mixt. for use with cement is formed of slaked lime mixed with paraffin or similar H_2O-repellant wax-like material.

Fireproof and insulating cement mixture. E. R. STOWELL. U. S. 1,382,329, June 21. A fireproof and insulating material adapted for use in building construction is formed of cement, Na silicate, powdered pumice and wood particles.

Hydrating lime. H. W. CHARLTON. U. S. 1,381,106, June 14. A hydrate of lime contg. less than the usual amt. of H_2O of hydration is prepd. by digesting slaked lime with an excess of H_2O under a pressure of 225 to 270 lbs. per sq. in. and at a corresponding temp.

Portland cement and calcining kiln. JOHN NELSON. Can. 212,734, Aug. 2, 1921.

Impregnating wood. L. N. LYON. U. S. 1,382,103, June 21. A body of tar, creosote oil or similar liquid for impregnating wood is heated to above 100° but below the temp. at which it would be liable to ignition. Wood is then immersed in the material until the moisture in the wood is converted into steam which escapes through the bath and the material of the latter serves as a sealing agent against reëntrance of moisture.

Seasoning wood with ozone. M. P. OTTO. U. S. 1,381,656, June 14. See Brit. 133,263 (*C. A.* **14**, 816).

21—FUELS, GAS, TAR AND COKE

A. C. FIELDNER

Fuel economies in Swiss gas works. PIATON. Soc. Tech. du Gaz. *Gas J.* **155**, 440(1921).—Swiss gas works consumed in 1913, 488,866 tons of coal and in 1918, 305,624 tons; in addition there were distd. 72,000 tons of wood and 20,000 tons of peat, the gas being enriched by C_2H_2 from 2,000 tons of CaC_2. In the Schlieren plant 4% of C_2H_2 was employed, representing 12% of the calorific value of the gas. The economies were effected from: (1) Waste heat of the products of combustion from the gas-furnaces; (2) red-hot coke on removal from the retorts; (3) gas-cooling plant. The waste heat from the gas-furnaces was used for raising steam in boilers, the necessary draft being obtained with an elec. fan. With a consumption of 13600 tons of coke in the producers annually, 15700 tons of steam at 7 kg. pressure were obtained, or 1.15 kg. of steam or 740 cal. per kg. of coke. By use of supplementary economizers with cooling of the products of combustion to 150°, a further 210 cal. were recovered. Recovery of the heat from the coke was effected in a Sulzer Bros. dry-quenching plant (cf. *C. A.* **15**, 2540). The production of satd. steam from this source per ton of coke was 300–420 kg. The water heated in the gas-cooling plant was used for feeding the boilers. At Zurich, 180 cal. were recovered per cu. m. of gas cooled; the temp. of the water in the coolers being 50–60°. J. L. WILEY

The origin and chemical structure of coal. FRANZ FISCHER AND HANS SCHRADER. *Brennstoff-Chem.* **2**, 213–9(1921); cf. *C. A.* **15**, 1610.—*Discussion.* KLEVER. The disappearance of the furan reaction does not necessarily imply destruction of cellulose residues. If the phenols of coal-tar arise from lignin residues and the humic acids of peat and lignite are also to be regarded as lignin derivs., these humic acids should give a phenolic tar on distn. W. Schneider showed that humic acid from lignite, forming about 50% of the latter, gave almost no tar on distn. The MeO and N content of humic acid is due to adsorption of lignin residues and albuminoids, the principal MeO content of lignite arising from the 10% of insol. org. residue. Cellulose is not as unstable as F. and S. supposed; peat beds more than 10,000 years old contain 15–25% of carbohydrates. The humic acids gradually increase in these beds as the carbohydrates decrease. Another objection to the theory of F. and S. is the known hydroaromatic character of coal tar as against the aromatic structure of lignin. These hydroaromatic hydrocarbons and alcs. (the latter change spontaneously to phenols) probably arise from the fossil resins of the coal bitumen. Unpublished work of Klever, Eisenhut and Forschner has shown that the "hydroaromatic phenols" of high mol. wt. polymerize to asphaltic substances even at 350° and at higher temps. give something like the "free carbon" of coke-oven tar. The aromatic hydrocarbons of coal tar probably arise from this source rather than by reduction of aromatic phenols. JONAS. Lignin isolated from wood shows no evidence of aromatic structure. The aromatic compds. obtained by F. and S. by pressure oxidation at 400° may have been formed by ring-closing from aliphatic compds.; the aromatic structure of coal is similarly due to the action of high temp. and pressure on the wood constituents. The formation of lignin in the plant is analogous to the formation of humus in the soil. Natural humic acids are mixtures of the true aliphatic humic acid with lignin. Sol. carbohydrates, such as would be formed by hydrolysis of cellulose are easily converted on the water bath to humic acids by dehydration and loss of HCOOH or CO_2. Hence principal peat constituents are lignin and the humus formed from cellulose. KEPPELER. Lignin-consuming bacteria are known, as well as cellulose-consuming species, and all bacterial life disappears in the deeper layers of peat beds. The peat formation at these depths must be a purely chem. process. Plants like moss contain large quantities (up to 70%) of carbohydrates which are not cellulose, and which probably have their own behavior in the peat-bed. FRANZ FISCHER and HANS SCHRADER. (Answer.) Pressure-oxidation of various fuels results in the following differentiation: cellulose and sugar give furan derivs. and no aromatic compds., while lignin, natural humic acid, lignite and coal give aromatics but no furan derivs. Artificial humic acid formed by concd. HCl from sugar gives both classes of compds. During the pressure oxidation lignin, peat, lignite and coal give brown humic acids from the very start, while cellulose does not; even at room temp. lignin takes up O_2 readily when moistened with an alkali, forming humic acids, differing in this respect again from cellulose. Formation of humic substances from cellulose during natural processes of decay has failed of demonstration. The high content of "carbohydrates" in peat, mentioned by Klever (*supra*), includes many other substances sol. in concd. HCl. Unpublished work by Tropsch has shown that vacuum distn. of Willstätter lignin gives 13.3% of tar which is almost entirely alkali-sol., and that 5 *N* HNO_3 nitrates it readily. Natural humic acid may be similarly nitrated, *hexanitrodiresorcinol* having been provisionally identified; alkali fusion gives phenoldicarboxylic acid, heating with aq. alkali under pressure, *m*-hydroxybenzoic acid. The low yield of tar from the distn. of isolated humic acid is ascribed to the rapid oxidation of the "protohumic acids" during the isolation; it is also known that coals rich in wax and resins yield less tar on distn. than those which are poor in these constituents. The remainder of the reply is polemical.

W. B. V.

Deterioration of the coking property of coal. WM. SEYMOUR. *Blast Furnace and Steel Plant* **9**, 435-7(1921).—Changes in coal after storage have heretofore been studied only for the heating value. Spontaneous internal heating has lately been found to cause deterioration in the coking property also. It was found that there is increase in wt., due to absorption of O, so that the H-O ratio drops rapidly. Data are given to show these changes. The tests prove that at 100° the coking property is destroyed. In making any test it should be considered that storage conditions differ from the recommended laboratory method in that (1) much coal is lump; (2) air has not free access and (3) storage piles contain H_2O vapor. Cannelton coal from W. Va. was investigated to det. the deterioration after submission to different temps. and times. A procedure was adopted from this study to predict the probable deterioration of any coal. To 5 g. of sample passing a 100-mesh screen is added 100 cc. of 10% HCl, the mixt. is boiled a few min., filtered, the residue washed with hot H_2O and the filtrate discarded. The residue is then washed with boiling *N* KOH to total a 50 cc. filtrate. The filtrate is compared with standard color Nessler solns. An empirical standard must be established. The brown color varies in depth with the extent of deterioration in coking property. Fresh coal gives no color. Results plotted with daily coke production show a remarkable correlation, and prove further that it is important to get coal to the ovens as soon as possible. C. C. DAVIS

Coal briquets. TEODORO CABRERA. *Rev. agr. com. y. trabajo* **2**, 386(1919); *Botan. Abstracts* **3**, 354.—Com. briquets are compared with those made with the resinous juice of *Enterolobium cyclocarpum* fruit; the latter prove superior. H. G.

Logical methods of utilization of Minnesota peat. H. H. HINDSHAW. *J. Am. Peat Soc.* **13**, 37-44(1920); *Botan. Abstracts* **4**, 271.—Modern methods of handling and treating increase the value of peat for various forms of fuel. H. G.

Willmarth peat fuel process. C. A. WILLMARTH. *J. Am. Peat Soc.* **12**, 113-22 (1919); *Botan. Abstracts* **3**, 446. H. G.

The present state and the future of the gas industry. The recovery of benzene. A. GREBEL. *Bull. soc. encour. ind. nat.* **133**, 602-38(1921); illus. E. J. C.

Report of gas incombustibles committee. JAMES H. GRAY, ET AL. *Gas J.* **155**, 484-6(1921); cf. *C. A.* **14**, 3148.—After taking of evidence (*Gas J.* **153**, 476, 548, 682, 754; **154**, 208, 276, 561), the Comm. recommends that "at present no limitation be placed on the proportion of incombustible constituents in town's gas, and after a period of 3 yrs. a further inquiry be instituted." Also in *Engineering* **112**, 351(1921). J. L. W.

Report of the carbon monoxide committee. WM. PEARCE, ET AL. *Gas J.* **155**, 429-31(1921); *Engineering* **112**, 318-20(1921); *Gas World* **75**. 168-71(1921); cf. *C. A.* **14**, 3148.—After taking evidence on the effects of CO in domestic gas (cf. *Gas J.* **153**, 407, 551, 684, 757), the Comm. has decided that "it is not necessary or desirable to prescribe any limitations of the proportion of CO which may be supplied in gas used for domestic purposes. Two reservations only are made: the way is left open for action of Parliament in case of unfavorable results, and no gas should be supplied which does not possess the distinctive pungent smell of coal gas. J. L. WILEY

Some critical obser ations on the generation of producer gas. I. Production of low-nitrogen gases in the gas producer. J. GWOSDZ. Charlottenburg. *Brennstoff-Chem.* **2**, 209-12(1921).—The continuous production of water gas in externally heated retorts has been attended with many technical difficulties, such as incomplete decompn. and high fuel consumption, while ordinary producer practice results in a gas high in inert constituents. G. reviews many of the proposals which have been made to produce a gas similar to water-gas by the use of O_2 or "Lindé-air" (enriched air), diluted with H_2O or CO_2, in the ordinary producer. Hempel's researches of 1901 (*Ver. zur Beförderung des Gewerbefleisses* 242(1902)), and Mezger's expts. with oil shale (*C. A.* **14**, 2700)

constitute the only actual exptl. work on the question which has appeared, and in both cases the results were disappointing partly because of the small scale on which they were secured. The proposals deserve to be tried seriously on a large scale. W. B. V.

Sulfate of ammonia plant at Leamington Gas Works. ANON. *Engine ring* **112**, 135–7(1921).—A detailed description of the plant and its operation. It exemplifies modern practice, and is very efficient in operation, producing 26.2 lbs. of sulfate per ton of coal. It can treat 56 tons of liquor daily. J. L. WILEY

Determination of benzene in coke-oven gas. I. A. THAU. *Blast Furnace and Steel Plant* **9**, 474–6(1921); *Glückauf* **57**, 505–11(1921).—A description with data of European methods of detg. C_6H_6 by absorption. C_6H_6 unlike other gases washed out cannot be successfully absorbed chemically, but only dissolved mechanically. Chem. detns. such as those of Harbeck and Lunge and of Dennis and O'Neill have been unsatisfactory. T. recommends a detn. wherein C_6H_6 is absorbed and weighed in an app. consisting of a train of absorption bottles. 15–20 cu. ft. of gas are aspirated for 3–4 hrs., first through picric acid to remove $C_{10}H_8$, then through $CaCl_2$ tubes, and finally through the C_6H_6 absorption train. The latter consists of 2 or more bottles of the Drehschmidt type as modified by Krieger, 22 cm. high, 5 cm. diam., surrounded by ice, and contg. fresh, boiled, clear paraffin oil. The detn. is done by direct weighing, and is professed to be very exact. C. C. DAVIS

The influence of drying lignite on the yield of low-temperature tar in its subsequent gasification. F. SEIDENSCHNUR. Berlin-Grunewald. *Brennstoff-Chem.* **2**, 241–4 (1921).—The author's experience had led him to doubt that the tar yield from dried lignite was as much smaller than that from raw lignite as found by Fischer, *et al.* (*C. A.* **15**, 1613). Lab. records of the briqueting industry showed the tar yield from the briquets (dried to approx. 15% H_2O) to be 93–97% of that from the raw lignite, as detd. in the Thuringian glass retorts. S. then constructed a gas-heated tube furnace designed for a 100-g. charge; the tar produced by it, using a CO_2-stream, was of good quality, and the tar yield was shown to range from 94 to 95% of the "theoretical," even with a bone-dry sample. F.'s low yields from dried lignite are attributed to decompn. by overheating, due to the shorter distn. time ($1^1/_4$ hrs. as against 4–6 hrs.) and the shape of his retort; the moisture in raw lignite would tend to prevent this overheating. W. B. V.

Composition of high- and low-temperature tars. HANS TROPSCH. Mülheim-Ruhr. *Brennstoff-Chem.* **2**, 251–2(1921).—Distn. of an Upper Schleswig coal at low temp. gave a tar containing only traces of solid organic acids, and the phenols were viscous, not solid. The low-temp. tar from coal of the same region, described by Marcusson and Picard (*C. A.* **15**, 3386), was probably exceptional. W. B. V.

Resins from phenols of low-temperature coal tar. W. GLUUD AND P. K. BREUER. *Ges. Abhandl. Kenntniss Kohle* **4**, 221–36(1919).—An investigation was carried out to det. what proportion of the total phenols in low-temp. coal tar could be utilized in the production of "bakelite" and "novolac" by condensation with CH_2O. The action of the latter in the presence of NH_4Cl as catalyst was tested on the following products: Crude tar from which the most viscous compds. had been removed, the fractions distg. between 150 and 250° and between 250 and 300°, including the hydrocarbons that distil at these temps., the cresol fraction, and the phenols obtained from the lubricating oil and resinous fractions. The hydrocarbons present did not interfere with the reactions and could readily be removed from the products, which were solid, brittle resins having the properties of the "novolacs." Condensation of a crude tar-cresol mixt. with benzaldehyde and paraldehyde yielded viscous semi-solid products which could be changed into solid resins by heating under pressure. The color of the resins varied, according to the material from which they were produced, from light yellow to dark brown, and they could be made less brittle by leaving behind in the final product a certain amt. of

the hydrocarbons originally present in the raw material. Bakelites *A* (sol.), *B* (fusible), and C (infusible) were prepd. by condensation in the presence of a basic catalyst such as NH_3, but variety *A* can only be made from the whole of the phenol fraction of the crude tar or from the whole of the crude tar itself. The bakelites are clear solid substances varying in color from light yellow to very dark brown, and the *A* variety yields good varnishes in 50% alc. soln. Variety *C* can be made from *A* by the use of benzylamine as a catalyst, or it can be produced directly from the phenol fraction boiling below 230° or from that boiling between 230° and 260° if soda is used as a catalyst.

J. S. C. I.

Blast-furnace gas poisoning (JOHANNSEN) **9.** Power from mercury vapor (EMMET) **13.** Utilization of ammoniacal gas waters as fertilizer (BONGIOVANNI) **15.** Producing low-boiling hydrocarbons (U. S. 1,381,098) **22.**

Liquid fuel. L. W. BATES. U. S. 1,382,456, June 21. A stable liquid fuel is formed of liquid hydrocarbons and dehydrated tar obtained from the cracking of oil vapors derived from the treatment of coal and oil or oil alone with steam.

Liquid fuel. L. W. BATES. U. S. 1,382,457, June 21. A stable mobile fuel is formed of incompletely miscible hydrocarbons such as mineral oils and dehydrated coal tar associated with particles of solid carbonaceous material, *e. g.*, pulverized coal.

Burning pulverized fuel. H. G. BARNHURST. U. S. 1,382,712, June 28. Pulverized fuel and air are introduced into a boiler furnace having a refractory lining and ignited. The fuel and the air are continuously supplied to maintain continuous combustion within the furnace and the deflagrating fuel and gases of combustion are passed through the furnace at such low velocity that at the point of travel of the gases through the furnace at which the highest temp. is reached the velocity will be substantially 7 ft. per sec. This low velocity avoids erosion of the refractory walls of the furnace and insures complete combustion of the fuel.

Fuel briquets from lignite. S. M. DARLING. U. S. 1,382,629, June 28. Lignite is mixed with about 10–12% its wt. of pitch and the mixt. is formed into briquets, which are heated to a temp. of about 370° and then cooled in the presence of the volatilized products evolved by the heating. About 12% of coal may also be used in the briquets.

Apparatus for indicating the condition of coal combustion. Z. OLSSON. U. S. 1,383,144, June 28. The app. comprizes an automatic recording device for indicating the % of CO_2 in flue gases.

Vertical retort for destructive distillation. L. F. SCHRADER, W. E. ROBERTS and V. BREDLIK. U. S. 1,382,746, June 28. A vertical retort adapted for the distn. of coal, lignite or peat is formed with an outer shell with heating flues having an inlet at the bottom and an outlet at the top and an inner shell with openings for carrying off gases. A diaphragm is provided near the lower end of the inner shell, forming a chamber for receiving the gases from the lower portion of the material, and a steam inlet is provided for supplying steam to the lower portion of the material to promote the formation of NH_3, which passes into the chamber mentioned.

Separating sulfur dioxide from gas mixtures. R. H. MCKEE. Can. 212,540, July 19, 1921. SO_2 is sepd. from gas mixts. by absorption in a silica gel. The dust and moisture are first removed and the temp. is reduced to below 25° and the gas is passed through the gel. The SO_2 may be removed from the gel by the use of a vacuum pump and passing a heated portion of the discharged SO_2 through the gel.

Suction gas-generator. J. FRANKLIN. U. S. 1,382,074, June 21.

Suction gas-generator. S. PHILLIPS. U. S. 1,382,118, June 21.

Coal-coking process. S. R. ILLINGWORTH. Can. 212,733, Aug. 2, 1921. Coal is heated to a temp. below 400° out of contact with air in order to destroy non-coke-

producing substances in the coal but to leave 5% by wt. of the resinous substance in the product.

Coke-ovens. F. JOHNSON and A. NORDQUIST. U. S. 1,382,916-7, June 28.

22—PETROLEUM, ASPHALT AND WOOD PRODUCTS

F. M. ROGERS

Petroleum laws of all America. J. W. THOMPSON. Bur. of Mines, *Bull.* **206**, 645 pp.(1921). E. J. C.

Preventable losses in petroleum refining. JOSEPH E. POGUE. *Chem. Met. Eng.* **25**, 442(1921). E. J. C.

Wastes and inefficient practices in the petroleum industry. W. A. HAMOR. *Chem. Met. Eng.* **25**, 441-2(1921). E. J. C.

Wasteful methods of the naval-stores industry. V. R. CROSWELL. *Chem. Met. Eng.* **25**, 440(1921). E. J. C.

Action of microörganisms on crude petroleum. J. TAUSZ. *Petroleum* **14**, 553-5 (1919); *Abstracts Bact.* **3**, 335-6.—A layer of petroleum from 1 to 2 mm. in depth was spread over a mixt. of ditch water with a soln. contg. 0.1% of Mg NH_4 phosphate, 0.08% of K_2HPO_4, 0.01% of $CaSO_4$, and traces of NaCl, KI, and $FeCl_3$. After several weeks the oil was found to have decomposed, and the liquid had become turbid with apparent formation of asphalt. With thicker layers of oil the action did not take place. Thin slices of paraffin wax placed in the nutrient soln. were also attacked, and the liquid became turbid. Expts. were made with refined and crude Russian and American lubricating oil and cylinder oil, and with the aid of pure cultures of microörganisms it was found possible to effect sepn. of the paraffin and naphthene hydrocarbons. Three new species of bacteria were isolated during the investigation. H. G.

Contribution to the knowledge of the composition of Swedish shale oil. GUSTAF HELLSING. *Arkiv Kemi, Mineral. Geol. Stockholm* **7**, No. 29, 23 pp.(1921).—Shale oils from various localities were examd. They were distd. from wrought iron cylinders of 20 l. capacity at a low red heat without the use of steam. The raw oil, brown in color, d. 0.9595 was fractionated at temps. varying from 75° to 330°, 25 fractions being taken. The higher-temp. fractions were found high in S. The 75° fraction gave qual. tests for acetone, though none was sepd. out by the usual methods tried. Dinitrotoluene was found upon nitrating fraction 118°–125°. Toluene was found in fraction 125°–132°. *p*-Trinitroxylene was sepd. from the 132°–145° fraction. Treatment with Br yielded dibromoxylene in the 145°–155° fraction. From the 155°–162° fraction sulfonation produced trimethylbenzenesulfonamide. Fraction 162°–175° yielded pseudocumene, which was also found in fractions up to 200°. In fraction 200° to 210° a tetramethylbenzene was found, while fraction 210°–225° yielded a dibromotetramethylbenzene. This high content of aromatic compds. definitely distinguishes Swedish shale oil both from Scotch and French shale oils. P. M. GLASOE

Turpentine, methanol and tar from tree stumps. FRANZ OTTO KOCH. Schöneiche. *Chem. Ztg.* **45**, 699(1921).—Too little investigation has been made up to date of the utility of stumps and roots as a source of relatively pure terpenes and oil of turpentine. Certain valuable components of the wood are volatile or are decompd. by sunlight or heat, so that previous processes for distg. dry wood are wasteful and inefficient. A new process patented by Franz Schmidt utilizes all components of the wood. Pine stumps by this continuous process produce approx. 5 kg. of turpentine, 1 kg. of MeOH and Me_2CO, 8 kg. of tar and 22 kg. of charcoal per 100 kg. of fresh stumps. C. C. DAVIS

Pipe-line transportation of hot oil. LEONARD L. BARRETT. *Chem. Met. Eng.* **24**,

1148–52(1921).—The design of oil pipe-lines with and without insulating coverings is considered. Heat losses from an uninsulated line are from 4 to 5 times greater than those from a line with a 1" covering of 85% magnesia. Use of d'Arcy's hydraulic formula, as modified by Durand, for spacing of heating and pumping stations, is illustrated. Curves showing changes of temp., pressure, viscosity, turbulence criterion, function, and density as a function of distance are given. By comparing an above-ground line insulated with $1^1/_4$" of 85% magnesia, with a bare ditched line, it is shown that the former has a greater thermal efficiency by $23^1/_2$% and stations need to be spaced only every 16.57 miles apart as compared with 13.73 miles for the buried uninsulated line. A numerical example shows that an 8" line carrying 25,000 bbls. of oil per 24 hours, covered with $1^1/_4$" of 85% magnesia and lying above ground, shows a capital saving of $72,000 per 100 miles of line, an annual saving of $36,700 per 100 miles, and a saving in the 1,000 barrel mile cost of 3.85c compared with an 8" ditched uninsulated line. A. R. ALBOUGH

Asphalt and related bitumens in 1920. K. W. COTTRELL. U. S. Geol. Survey, *Mineral Resources of U. S. 1920*, Part II, 45–53 pp. (Preprint No. 7, published Aug. 25, 1921). E. J. C.

The preparation and care of a tar pit. C. E. EKLÖF. *Skogen* **6**, 189–210(1919); *Botan. Abstracts* **4**, 62.—The process of ext. tar from pine stumps is described in considerable detail. The yield is from 20 to 30 l. of tar per cu. m. of wood. Charcoal is obtained as a by-product in amt. equaling 5 or 10 % of the original vol. of the wood. H. G.

The lumber industry—a flagrant waster. EARLE H. CLAPP. *Chem. Met. Eng.* **25**, 446–7(1921). E. J. C.

The lack of team work in the wood-distillation industry. FRANK J. ROOT. *Chem. Met. Eng.* **25**, 448(1921). E. J. C.

Commercial utilization of cotton stalks (ANON.) **23.** Geology of the Cement Oil Field, Okla. (REEVES) **8.** Oil prospects in Washington Co., Utah (BASSLER, REESIDE) **8.**

Cracking petroleum hydrocarbons. D. W. HOGE. U. S. 1,382,727, June 28. Petroleum from which free gasoline has been removed is vaporized in a still and the vapor is conducted to a cracking app. and sufficiently heated to effect cracking of the hydrocarbons into products of lower b. p. The highly heated cracked vapor is led from the cracking app. to a sep. receptacle contg. a bath of petroleum contg. free gasoline and passed through the bath, to heat it and distil off the free gasoline, and the mixed vapors thus produced are led to a condenser. Residuum is withdrawn from the still.

Producing low-boiling hydrocarbons. C. M. ALEXANDER and G. H. TABER, JR. U. S. 1,381,098, June 14. Hydrocarbons of high b. p. such as gas oil, fuel oil or coal tar distillates of high b. p. are converted into products of lower b. p. by heating their vapors with vapors of $AlCl_3$, $FeCl_3$, or $ZnCl_2$.

Retort for distilling oil-shale or similar materials. S. SCHIEFFELIN. U. S. 1,381,936, June 21. Oil shale or similar material to be distd. is heated within a horizontally disposed open-ended spiral pipe retort which is revolved so as to dip up material at one open end and discharge it at the other. An axial outlet for vapors is provided intermediate the ends of the spiral and the latter is mounted within a heating chamber in which some pressure may be maintained, sufficient to prevent escape of vapors except at the outlet.

Apparatus for distillation of oil shale. E. E. HEDGES. U. S. 1,383,205, June 28. The material undergoing distn. is passed through a horizontally disposed but slightly inclined retort.

Re-run petroleum still. D. PYZEL. U. S. 1,383,024, June 28.

Apparatus for dehydrating petroleum oils by electric treatment. H. R. QUINBY. U. S. 1,382,234, June 21.

23—CELLULOSE AND PAPER

A. D. LITTLE

Commercial utilization of cotton stalks. ANON. *Bull. Imp. Inst.* **19**, 13–8(1921).—Cotton stalks from the Punjab and Central Provinces, India, were examd. with the following results: moisture 10.2 and 10.7%, cellulose 44.1 and 40.3%, and ash 2.6 and 3.0%, resp. These stalks treated with NaOH under conditions similar to those employed in the manuf. of paper on a com. scale yielded 41 and 34% dry pulp, resp. A paper pulp of fair quality which could be bleached to a pale cream tint resulted. Dry distn. of the stalks yielded 35.4% charcoal and 41.1% crude pyroligneous acid. The total tar yield was 10.2% and the total yield of CH_3COOH was 3.4%. The charcoal did not compare very favorably with lampblack or C black and would rank only as a fuel charcoal. The yield of wood naphtha (1.5%) is about the same as is obtained from hard wood but the acid yield is slightly less. The stalks are, however, such a bulky material that they would require large retorts for treatment even if cut up and compressed. R. L. SIBLEY

More pulp per cord of wood—why not? JOHN D. RUE. *Chem. Met. Eng.* **25**, 447–8(1921). E. J. C.

New Zealand waste timber for paper making. ANON. *Bull. Imp. Inst.* **19**, 1–10 (1921).—Results of the examn. of 8 New Zealand woods show that 4 species of *Fagus* (*Nothofagus*) yielded pulps of similar character which bleached readily and furnished fairly strong papers of good quality. The yields of pulp were 41.5 to 44.0%, that from *F. fusca* being the best. The *Beilschmiedia Tawa wood* gave a yield of 42.5% pulp and yielded paper of similar quality to that obtained from the species of *Fagus*. The *Weinmannia racemosa* wood gave a rather low yield of pulp (36.5%) which, however, bleached satisfactorily and had good felting properties. The strongest papers were obtained from the weeds of *Pinus Laricio* and *Pinus radiata* but the pulps from these weeds did not bleach quite so readily as those from the other 6 samples. The yields of pulp were only fair (39%). R. L. SIBLEY

Papyrus as paper-making material. L. VIDAL AND M. ARIBERT. *L'agronomie coloniale* **6**, 53(1921); *Bull. Imp. Inst.* **19**, 81–2(1921).—The air-dry stems contained 15% moisture and yielded 47% of cellulose, 2% ash, 3.4% fatty substances and 4.3% H_2O sol. matter. The material, after treatment with steam at 1–2 atms., was heated with 13% NaOH of 6° Bé. strength for 6.5 hrs. The yield of pulp was 40% and could be easily bleached. Paper made from the pulp was of very good quality. R. L. S.

West African corkwood. ANON. *Bull. Imp. Inst.* **19**, 10–3(1921).—The tree yielding the cork wood was the *Musanga Smithii* ("umbrella tree"). Expts. showed it to be unsuitable for use for making artificial limbs because of the shortness of the grain. The wood contained 8.8% moisture, 0.6% ash and 51.5% cellulose, and when treated with 20% NaOH for 8 hrs. at 160° the yield of dry pulp was 50%. It is, then, a promising material as a source of paper pulp. R. L. SIBLEY

Investigation of hop fibers (SCHWEDE) **25.** The prickly pear. Possibilities of its utilization (JURITZ) **12.** Waterproofing composition (U. S. pat. 1,383,068) **18.**

Enamel for paper. R. HEIM. U. S. 1,381,991, June 21. Enamels for use on paper are formed of pigments, size and oil reduced to a putty-like condition: *e. g.*, lime putty, clay and oxidized oil.

Rosin size solution. J. A. DeCew. U. S. 1,382,346, June 21. A sizing adapted for use on paper stock is formed of a drying oil such as linseed or tung oil, soap made from tung, linseed or other drying oil, rosin and rosin soap.

25—DYES AND TEXTILE CHEMISTRY

L. A. OLNEY

Key index for dyestuff intermediates. W. N. Watson, A. R. Willis and R. N. Shreve. *Color Trade J.* **8**, 189–93, 234–9; **9**, 35–9, 79–84, 118–22(1921). E. J. C.

Some investigations concerning ingrain dyestuffs. A. J. Hall. *Textile Colorist* **43**, 589–90(1921).—A discussion, with several formulas, of the methods for producing aniline black, para-red, nitroso blue, paramine brown and other less common insol. pigment dyestuffs. Chas. E. Mullin

Biochemistry of the indigenous indigo dye vat. Gilbert J. Fowler and M. Srinivasiah. *J. Indian Inst. Sci.* **4**, 205–21(1921).—"In the dye vats employed in Bangalore and generally in the south of India a species of seed is the fermenting agent, about 9 lbs. of seed being added to the vat per one lb. of indigo of about 50% indigotin content." The object of this study was to det. the nature of the fermentation set up by the seeds as preliminary to the scientific control of the process. The expts. included a chem. and histological examn. of the seed in question which was from the plant *Cassia tora*, order *Leguminosae;* a study of the bacteria occurring in the seed; and studies of the fermentation under special lab. conditions. The expts. are described with much detail and the following conclusions stated: The seeds of *Cassia tora* carry bacteria which ferment the mucilaginous content of the seeds with the evolution of H and CO_2. This H in the nascent state is the effective agent in reducing the indigo. The reduction is assisted by the fact that the indigo is held in suspension by the mucilage while this is undergoing fermentation. The seeds contain a bitter principle which exercizes a selective antiseptic effect on the bacteria occurring in the seeds, so that practically only one species is present. So long as there is a sufficient supply of *Cassia tora* seeds, a reasonably pure culture is assured and a special technic to obtain such a result is unnecessary. This selective antiseptic effect appears to be a general phenomenon and has been observed in the case of paddy (rice in the husk, cf. Fowler and Scn, *J. Indian Inst. Sci.* **4**, 145). It is evidently of importance to the life of the seed and extended research work on the subject is in contemplation. In the case of *Cassia tora* although the plant grows on barren soil the seed has a high percentage of N. It is noted that organisms from a medium in which N fixation had occurred were not inhibited by the bitter principle, apparently therefore the organisms on the seeds play some part in N fixation. L. W. Riggs

Feeding dyestuffs to silk worms. W. F. Edwards. *Textile World* **60**, 1111–3 (1921).—A review of the exptl. work upon dyeing silk by this method. C. E. Mullin

Dyestuff testing in the textile industry. Edw. Wallace Pierce. *Can. Dyer and Color User* **1**, 132–6(1921).—Methods of testing the strength of the various dyes. Chas. E. Mullin

Cause of waste in the textile industry. Anon. *Chem. Met. Eng.* **25**, 436(1921). E. J. C.

The microscopy of textiles. Frederick J. Hoxie. *Mech. Eng.* **43**, 592–3(1921). E. J. C.

The textile laboratory and its equipment. Chas. L. Howarth. *Am. Dyestuff Rep.* **9**, Sec. 2, No. 10, 33–5(1921); illus. E. J. C.

Scroopy effects on cotton, woolen and silk goods, with possible future changes. Raffaele Sansone. *Textile Colorist* **43**, 591–5(1921).—The various methods used

for producing these effects are discussed. On silk they are obtained by: treating the boiled off, slightly rinsed and hydroextracted silk with a weak acid bath; dyeing with acid colors, the bath contg. an excess of acid; dyeing in a boiling off soap bath which has been broken by acid; treating the dyed material with a soap bath and then with a weak acid bath; S bleaching the gray boiled off silk; treating the boiled off goods with an aqua-regia bleaching bath; or, treating the gray goods with an acid peroxide bleaching bath. The effects on wool are obtained by boiling in a weak bath of H_2SO_4, HCl, AcOH or formic acid, either before, while, or after dyeing, or while fulling or milling. On cottons the effects are obtained by org. or mineral acid processes; tannic, boric, and fatty acid processes. Several formulas are given. CHAS. E. MULLIN

On the deterioration of cotton on wet storage. NANCY FLEMING AND A. C. THAYSEN. *Biochem. J.* **15**, 407–14(1921); cf. *C. A.* **14**, 1899.—When raw cotton contains a large number of microörganisms it may be assumed that the cotton has been exposed to damp. With the help of a "swelling test," based on Balls' observation that treatment with CS_2 and alkali causes the cotton fibers to swell, thereby rendering the structure of the fibers visible under the microscope, a method has been worked out for the quant. detn. of the bacterial deterioration of cotton. BENJAMIN HARROW

Effect of certain fireproofing solutions on cotton fabric. R. L. SIBLEY. *J. Ind. Eng. Chem.* **13**, 676–7(1921).—Seven different fireproofing solns. were tested upon tire fabric and after drying the breaking strength of each sample was detd. The alum and Na_2CO_3 treatment tendered the fabric so that it was easily torn by the fingers. $Na_2B_4O_7$ with NH_4Cl, $MgSO_4$ or glucose tendered the fabric from about 20 to 45%. A 15% soln. of sodium tungstate ($Na_2WO_4.2H_2O$) slightly weakened heavy fabrics and slightly strengthened light fabrics. A 3.5% soln. of sodium tungstate was found to have the least weakening action and is therefore recommended. L. W. RIGGS

Water resistance of treated canvas during exposure to weather. F. P. VEITCH AND T. D. JARRELL. *J. Ind. Eng. Chem.* **13**, 672–6(1921).—Eighteen tests with suitable controls were made with various combinations of amorphous mineral wax, beeswax, paraffin, rosin, Cu oleate, Pb oleate, Bermudez asphalt, petroleum asphalt, wool grease, Japan wax, and candelilla wax, using 2 or 3 of these waterproofing materials in each formula. The tests were made on 12-oz. U. S. standard gray duck. Some of the conclusions are as follows: All of the treatments increase the water resistance of canvas sufficiently for use as permanent tops or covers which lie smooth. When Pb oleate is included in the formulas the water resistance is increased. Bermudez asphalt or petroleum asphalt is fully as good as Pb oleate. Cu oleate is not as effective. Beeswax is better than any of the other hard waxes used, including paraffin and ceresin. Amorphous mineral wax is a better waterproofing agent than paraffin. Wool grease is a useful constituent in formulas containing other waterproofing agents, but amorphous mineral wax may be substituted for wool grease without loss of water resistance. Both the funnel and spray tests applied to newly treated duck indicate higher water resistance than is actually found in service. When a treatment secured the max. rating by both the funnel and the spray tests, it also received a high rating in the service test. Paraffin, Japan wax, ceresin, candelilla wax, and rosin were not effective waterproofing materials, they lacked durability. L. W. RIGGS

Effect of iron in the lime boil. ELTON R. DARLING. *Textile World* **60**, 1215–7 (1921).—The result of 12 exptl. boils on cotton goods with about 2% lime, contg. from a trace to as much as 10.82% Fe_2O_3, shows that very little Fe was taken up by the goods from lime contg. as much as 6.45% Fe_2O_3. The CNS test shows a little more Fe in the goods from the 3 boils with lime contg. 8.31–10.82% Fe_2O_3. No change in color of the goods was noted even with the lime of highest Fe content. D. thinks that the danger due to a trace of Fe in lime for the boil has been much overestd. CHAS. E. MULLIN

A viscosity method for testing diastase products. A. J. HALL. *Can. Dyer & Color User* **1**, 156–61(1921).—Diastase for use in stripping starched fabrics is evaluated by detg. the change of viscosity produced in a 3% potato starch soln. by the action of a definite quantity of 0.4% soln. of diastase at 21–2° for 40 min. A very simple app. and procedure are described. CHAS. E. MULLIN

More about lupine fibers. R. SCHWEDE. *Jahresber. Ver. angew. Botan.* **16**, 14–8(1918); *Botan. Abstracts* **7**, 280.—A discussion of the relative value of various species of *Lupinus* as a source of com. fiber. S. describes results of microchem. tests for cellulose, lignin, etc., and compares his results with those of Hanausek. Of the 3 species which he finds available in sufficient quantity to be of use in the present crisis, he considers the fibers of *Lupinus albus* less suitable than those of *L. lutens* and *L. angustifolius*. H. G.

Investigation of hop fibers. R. SCHWEDE. *Jahresber. Ver. angew. Botan.* **16**, 8–13(1918); *Botan. Abstracts* **7**, 280.—A microscopical and chem. investigation of the bast fibers and adjacent tissues of the hop plant (*Humulus lupulus* L.). S. finds that the morphological characters are much the same as for other members of the Urticaceae. He believes that the qualities of the fiber are such that they could be used in the manuf. of textiles at least under stress of such conditions as existed during the world war. The fiber was successfully used in the manuf. of paper. H. G.

Wool oils. JAMES B. MCARTHUR. *J. Textile Inst.* **12**, 302–5(1921).—Wool oils may be from 3 main sources: animal, vegetable, or mineral, or from mixts. of these. For certain classes of work olive oil is the best. Drying oils are unsuitable for wools when they are to be stored in the grease, owing to their tendency to combine with O and make the yarn sticky and yellow. The use of drying oils also develops so much heat as to cause spontaneous combustion. The Mackey test indicates whether the oil is dangerous. Fourteen g. of the oil are distributed over 7 g. of cotton, loosely packed in a cylinder of wire gauze, which is placed in an air oven heated by boiling water. If the thermometer reaches 400° F. in less than 2 hrs. the oil is dangerous. Mineral oils when blended with fatty oils up to 50% are satisfactory as wool oils. They are removed with greater difficulty but they are not likely to cause fires in the wool. About 70 yrs. ago there was introduced the use of oleic acid made by autoclaving fats and removing the solid acids by pressing. The great advantage of this is the easy sapon. with Na_2CO_3 and subsequent easy removal by washing out. One defect of these wool oils is that they are thinner and less viscous than olive oil and are thus more liable to fly off as a fine spray in rapidly revolving cards. This is overcome by converting $^1/_{20}$ of the oleic acid into soda soap. Recovered oils from the suds can be used for lower grade oils or can be enriched by the addition of oleic acid to make them fit for re-use. E. S.

Acidity and basicity (KELLER) **2**. Report of the Imperial Agricultural Bacteriologist (HUTCHISON) **15**. The prickly pear. Possibilities of its utilization (JURITZ) **12**. Waterproofing composition (U. S. pat. 1,383,068) **18**.

Azo dyes. C. JAGERSPACHER. U. S. 1,382,196, June 21. By combining aromatic *o*-hydroxydiazo compds. with a α-hydroxynaphthalenemonosulfocarboxylic acid (which combines with the diazo compds. in the *o*-position to the OH group without splitting off the latter) there are obtained azo dyes which dye on mordants and which are especially adapted for printing on cotton. The dyes are dark powders which dissolve in H_2O with red to violet colorations. They dye wool in an acid bath red to brown and violet tints becoming, on subsequent chroming, red to violet, fast to fulling and to potting; they produce red to violet prints fast to soaping, Cl and light when printed on cotton with Cr mordants. Among the starting materials which may be used in forming

the dyes are: the diazo deriv. of 4-nitro-2-amino-1-hydroxybenzene-6-carboxylic acid and 1-hydroxynaphthalene-3-sulfo-6-carboxylic acid; and 4-sulfo-2-amino-1-hydroxybenzene-6-carboxylic acid and 1-hydroxynaphthalene-3-sulfo-5-carboxylic acid.

Universal gray dye. CHAS. C. HUFFMAN. Can. 212,314, June 28, 1921. A gray dye soap is formed by combining an oil and an excess of a saponifying agent, then adding phenol black dissolved in hot water to the sapon. soln. just before sapon. is complete.

Sulfur-black. A. C. BURRAGE, JR. and G. MEISEL. U. S. 1,383,071, June 28. In prepg. sulfur-black, H_2O of suspension is filtered from the solid color, and the H_2O remaining associated with the dye is partially evapd. to obtain a product of a moist powdery consistency.

Sulfur-black. A. C. BURRAGE, JR. and G. MEISEL. U. S. 1,383,072, June 21. Solid comminuted NaCl is mixed with sulfur-black associated with H_2O, in order to produce a sol. product of standardized quality.

Waterproofing composition. S. C. GRAVES. U. S. 1,382,077, June 21. A waterproof compn. adapted for coating fabrics is formed of denatured alc. 2 oz., C_6H_6 0.5 oz., acetone 5 drams, pyroxylin 1.5 drams and corn starch 3 drams.

Dyeing animal fiber. J. H. FIEBIGER. U. S. 1,383,092, June 28. An org. acid such as oxalic acid (to an amt. not to exceed 5 times the quantity of the dye) is mixed, together with Na_2SO_4 or other suitable diluent, with aniline acid coloring substances such as acid blue black in order to obtain a compn. for dyeing wool, silk or *kid leather*.

Dyeing machines. WM. A. AINSWORTH. Can. 212,256, June 28, 1921. A dyeing machine has means for transferring yarn from one holder to another over a reservoir contg. color in which a roller is mounted for rotation; the roller is provided with liquid-absorbing material and means for intermittently pressing the yarn into contact with the absorbing material.

Machine for dyeing fur skins. DICKERSON. Can. 212,472, July 12, 1921.

Apparatus for bleaching or dyeing cloth. M. POETZSCH. U. S. 1,383,021, June 28.

Fabric for airships. H. A. GARDNER. U. S. 1,381,412, June 14. Multiply rubber-coated fabric for gas receptacles is provided with an exterior coat of polymerized tung oil and resin. U. S. 1,381,413 relates to a similarly coated fabric, the cloth of which is treated with a fireproofing substance such as NH_4 phosphate. Al powder is also used in the coating.

Bleaching vegetable fibers. G. G. TAYLOR. U. S. 1,381,440, June 14. Materials of vegetable fibers are bleached by treatment with a hypochlorite together with less than an equimol. proportion of boric acid.

26—PAINTS, VARNISHES AND RESINS

A. H. SABIN

Improving the paint and varnish industry. ROBERT S. PERRY. *Chem. Met. Eng.* 25, 444–5(1921). E. J. C.

Waste in paint and varnish oils. OTTO EISENSCHIML. *Chem. Met. Eng.* 25, 444 (1921). E. J. C.

Ultramarine pigments. AUGUST CHAUDET. *Anales soc. quim. Argentina* 8, 100–4(1920).—C. cites the following expts. to support the belief that the ultramarines are solid solns. of S: If kaolin be treated with a hot concd. soln. of Na polysulfide a blue color is produced. By using either natural or artificial Na Al silicate instead of kaolin a much more intense blue is produced. If to a boiling concd. soln. of Na polysulfide an excess of dry hydrated silica be added an intense blue or violet color is produced. Slaked lime and cold concd. Na polysulfide give a blue or green color, $Mg(OH)_2$ gives the same result and so does dry starch. L. E. GILSON

Use of lead compounds of phenols [in paints]. F. FISCHER AND V. EHRHARDT. *Ges. Abhandl. Kenntnis Kohle* **4**, 264–79(1919).—Pb oxide combines with phenol, cresol, *p*-hydroxydiphenyl, and naphthols in benzene soln. to give products which are not very satisfactory as paints. If, however, instead of the pure phenols the crude phenol-rich fraction (middle oil) of low-temp. tar or coke-oven tar is used, the product is a useful paint for protecting iron-work from rust. The difference in the two products is ascribed to the action of the resinous substances produced from the easily oxidizable hydrocarbons in the crude oils by the action of the Pb oxide. Oxidation of the crude tar oils and distn. with $KMnO_4$ or HNO_3 yields varnish-like substances. J. S. C. I.

Improved process of refining linseed oil. ALEX. SCHWARCMAN. *Chem. Age* (N. Y.) **29**, 280–2(1921).—After the soda treatment of linseed oil, soaps and impurities are usually allowed to settle or they are washed out with dil. HCl; but the settling process is wasteful, and the washing with acid produces a less desirable oil. S. overcomes these disadvantages by agitating the oil with just about enough NaOH soln. to neutralize free fatty acids. It is then heated to 180° F. and washed 5 or 6 times until neutral with hot H_2O. Sepn. of the aq. layer containing all albuminoid bodies and soaps takes place quickly. The oil is then dried *in vacuo*, and bleached with fuller's earth or boneblack. This process produces a very high grade neutral "varnish" oil. If a refined oil of somewhat acid nature is required, free fatty acids are added in suitable quantity. A diagram of the app. is given. F. A. WERTZ

The mechanism of the oxidation of drying oils as elucidated by a study of the true oxygen absorption. (I). Linseed oil and its fatty acids. SAMUEL COFFEY. *J. Chem. Soc.* **119**, 1152–61(1921).—Curves representing the gain in wt. of linseed oil films on exposure to air show only the apparent O absorption because of a simultaneous loss of volatile products. The app. used by C. to det. true O absorption is a modification of that used by Genthe (*Z. angew. Chem.* **19**, 2087(1906)). Broken pumice satd. with H_2SO_4 is placed in the bottom of a large flask; the end of a stick of NaOH wrapped in Cu gauze is fitted into a glass cup, and the stick is then lowered cup first into the flask; filter paper contg. the oil film is finally suspended from the stopper of the flask. The oil film is prepd. by satg. a 11-cm. filter paper with a known vol. of a standard soln. of pure raw linseed oil in petroleum distillate, b. p. 40–60°. Immediately after the oil film is in place, the flask is filled with H and placed in a thermostat at 100°. After constant temp. is reached, the H is replaced by O, and the absorption of the film detd. by noting changes in pressure within the flask, read every 0.5 hr. Absorption of O commences fairly rapidly after about 15 min. and then gradually diminishes in velocity until complete after 6 hrs. With widely varying amts. of oil, results concordant to within 1% show that linseed oil absorbs a mean of 28.7% O; and linseed fatty acids, 30.09%. Volatile products from oil oxidized in air at 100° showed strong positive reaction of H_2O_2. Oxidizing the oil in O at 100° and absorbing the volatile products in $Ba(OH)_2$ showed CO_2 equal to 5.4% of the original oil, equivalent to 3.9% O; and volatile carboxylic acids, present chiefly as AcOH, also equivalent to 3.9% O. The total true O absorption of linseed oil is greater than that called for by the theory of molecular autoxidation (*i. e.*, addition of O at the double linkages), by an amt. approx. equivalent to the O found in the volatile products. This indicates that while the primary reaction in the oxidation of linseed oil is molecular autoxidation, there is a further "excess" oxidation. The glyceryl radial appears to have no effect on the mechanism of the oxidation reactions, but the free fatty acids oxidize more rapidly. Results with oils contg. driers are not comparable with raw oils. F. A. WERTZ

The resin industry: utilization of sand wastes. S. L. K. *Australian Forest J.* **3**, 172–5(1920); *Botan. Abstracts* **7**, 117.—A brief discussion of the resin industry, and a short description of the methods of collecting and refining resin. H. G.

Soy bean oil (FELLERS) **27.** Resins from phenols of low-temperature coal tar (GLUUD, BREUER) **21.** Fabric for airships (U. S. pat. 1,381,412) **25.**

Paint. F. L. BUCHANAN. U. S. 1,381,274, June 14. A paint adapted for use on roofs is formed of talc 9 lbs., Fe pyrites 4 lbs., SiO_2 4 lbs., granite 4 lbs., limestone 4 lbs., hematite 75 lbs. and suitable amts. of oil, varnish and thinner.

Fire-resisting and waterproof paint. G. BLENIO. U. S. 1,382,617, June 28. A filler for manuf. of fire-resisting waterproof paint is formed of calcined magnesite 15, $CaCO_3$ 25, china clay 30, $Ca(OH)_2$ 7 and a binder composed of casein 14, neutral soap 3 and a waterproofing compd. such as Ca stearate 6 parts.

Litharge and red lead. H. M. GABEL. U. S. 1,382,282, June 21. Comminuted metallic Pb is repeatedly and successively brought into contact with an oxidizing gas such as heated air and subjected to an abrasive action, the oxidizing gas being successively heated to effect drossing of the Pb and production of PbO or Pb_3O_4.

Ink. H. and W. C. KRUSE. U. S. 1,381,648, June 14. An ink adapted for use on mimeographs is formed of an alumina black lake 10, glycerol 40, Turkey red oil 60 and alumina brown lake 2.5 parts.

Removing varnish. G. H. MAINS. U. S. 1,381,485, June 14. Furfural is applied to varnished surfaces to loosen the varnish and facilitate its removal.

Linseed-oil substitute. M. DARRIN. U. S. 1,382,345, June 21. A liquid mixt. adapted for use as a substitute for linseed oil in paints is formed of a soln. of heat-polymerized coumarone resins in solvent naphtha mixed with linseed, Chinawood or other oils.

Linoleum. G. W. PRIEST. U. S. 1,381,737–8, June 14. Polymerization products of the coumarone or indene series are mixed with an oil or oxidized oil such as tung or linseed oil at a temp. of about 100° or lower in order to form a compn. suitable for the manuf. of linoleum. Cf. *C. A.* **14,** 1450.

Rust-proofing composition. W. R. EMIG. U. S. 1,381,112, June 14. A mixt. for rust-proofing metals is formed of gilsonite 7, kauri nubs 7, Chinawood oil 5⅔, turpentine 5, mineral spirit 43, Japan drier 1, asbestine 6⅓, lampblack 6⅓, lithopone 6⅓, black Mn oxide 7⅓ and a mixt. formed of H_3PO_4 and Fe filings 5 parts.

Artificial varnish resin. C. ELLIS and H. M. WEBER. U. S. 1,381,863, June 14. A resinous product suited for use in grinding varnishes with pigments is formed of fusible copal resin, ordinary rosin and glycerol, heated together to 270–310°.

Coating concrete floors. C. ELLIS. U. S. 1,383,268, June 28. Dusting of cement concrete floors is prevented by coating them with a coumarone resin having a m. p. above 75°.

27—FATS, FATTY OILS AND SOAPS

E. SCHERUBEL

Decolorizing agents for the fat industries. J. ZIFFERER. *Oel- u. Fettind.* **2,** 63–4, 87–8, 112–13, 134, 160, 183–4(1920).—The only suitable carbons are those made from materials which do not fuse on charring; hence proteins, glue, etc., give the best products when carbonized with K carbonate or Na K carbonate. Carbons contg. N are more active than those contg. none. In diminishing order of activity the chief carbons are: animal charcoal from ferrocyanide residues, blood charcoal, bone charcoal, glue charcoal, soot, wood charcoal, and sugar charcoal. Nodules of the size of peas should be used for aq. solns., but for oils finely ground C is best. For the fat industry bone char is of much less importance than charcoal from ferrocyanide manuf.; the latter cannot be revivified. Florida fuller's earth (*floridin*) is active in the air-dry state at

18°, but more so at 120° or when dehydrated at 300–400°. The oil is treated with 2–5% and warmed. The earth can be revivified by various methods, but it recovers only two-thirds of its original activity. Salad oils decolorized by silicates often have a slight rancid flavor, and for this reason $NaHCO_3$ is frequently added. An earthy flavor is eliminated by washing with 10% brine. J. S. C. I.

Basic technical information needed by the edible oil industry. JOHN C. INGRAM. *Chem. Met. Eng.* 25, 438–9(1921). E. J. C.

The manufacture of pure hydrogen and the catalytic hydrogenation of oils. E. B. MAXTED. *J. Soc. Chem. Ind.* 40, 169–72T(1921).—Four methods are used for the industrial generation of H for use in catalytic processes, *viz.*—(1) Electrolysis of H_2O; (2) low-temp. sepn. of the constituents of water gas; (3) catalytic water-gas process, involving the replacement of CO by H, by reaction with steam in the presence of a catalyst; and (4) the cyclic water-gas process in which the replacement of CO by H is carried out in 2 sep. phases. Of these the gas from the 1st and last can be used directly for catalytic work, while the gas from the 2nd and 3rd requires the removal of CO. The cyclic water-gas method is particularly suitable for making H for hardening oils. In its primitive form this method consists in making H by the action of steam on heated Fe, the resulting oxide being subsequently reduced to metal by means of water gas. H made by this process contains a small amt. of CO which does not originate from the residue of reducing gas but is produced continuously during the steaming period. During the reducing period, the contact mass, in addition to becoming reduced, causes the catalytic decompn. of the CO into CO_2 and C; the C deposited reacts with steam forming CO. This deposition of C may be prevented if the reducing gas contains CO_2 in excess of the equil. % corresponding to the equation $2CO \rightleftarrows CO_2+C$. The difficulty is solved by using a gas such as is obtained from a water-gas producer operating at an abnormally low temp. By purifying this gas by means of a scrubber and hydrated Fe oxide and the H by a mixt. of lime and Fe oxide, H of 99.9% purity can be obtained. The course of the absorption of H during hydrogenation at a given temp. was formerly thought to follow the unimol. reaction law, but Armstrong and Hilditch have shown that the gradual diminution in the velocity of absorption as satn. proceeded is not obtained with substances which are free from inhibitants, the true reaction curve following the linear equation up to a point near complete satn., when the rate of H absorption quickly drops to 0. This would seem to indicate that the reacting system consists of a complex in which the concn. of the unsatd. substance is const. as long as a supply of this is available. In practice, oils of ordinary purity give non-linear reaction curves. In the earlier plants using Ni oxide, temps. of 200° to 250° were used; but these temps. influence the quality of the product and speed of reaction adversely. The optimum temp. will depend on the nature of the Ni catalyst and the oil to be treated. Tests made with olive oil show that the temp. of max. activity is about 175° although activity is appreciable at 80° and sufficient for efficient hardening at 100° with relatively pure oils. In plants controlled by M. hardening is begun at about 120° to 130° and goes to 160°. The rate of absorption of H at a const. temp. was shown by tests to vary directly as the pressure. The hardening vessel of a com. hardening plant which M. operates consists of a relatively narrow portion made of steel plates welded and terminating in 2 broad chambers. In place of movable agitators the narrow portion contains a series of stationary propeller-shaped baffles, the blades of which are curved in such a manner that a substance on being projected through this cylinder is rotated alternately in a clockwise and anti-clockwise sense by successive baffles; the charges of oil and of H with which the vessel is filled are projected at a high velocity through the central column in opposite directions by means of pumps. A vessel to hold 2 tons has a height of 22 ft., the upper and lower reservoirs being 4½ ft. The heating of the charge is effected by means of a steam

jacket. The pressure of the H used is from 40 to 80 lbs.; and not more than 30 min. is required to harden peanut oil to a brittle fat, 1% Ni catalyzer being used. E. S.

Raisin-seed oil. Émile André. *Compt. rend.* **172**, 1413–15(1921); cf. *C. A.* **15**, 3404.—The acetyl no. of raisin-seed oil is the most variable const. of this oil and it appears that acid alcs. similar to those of castor oil are present. A. has tried to isolate these by well-known methods without success. The fatty acids of raisin-seed oil are sepd. into 3 groups and the acid alcs. concd. in one of them by the following method: 125 g. of oil are mixed with 150 g. of alc. at 90° in a flask and 35 g. of NaOH in enough water to make 100 cc. added with agitation. After 15 to 20 min. the mixt. whose temp. is about 40° has become homogeneous and it is then poured into 1250 cc. of water and shaken out with ether 3 times. The ether solns. are combined and evapd. after drying with Na_2SO_4. This unsapond. residue is set aside. To the soap soln. 125 g. of H_2SO_4 dild. $^1/_2$ are added. The fatty acids are sepd., dried over Na_2SO_4, and then dissolved in 3 l. of alc. at 70°, to which 40 g. of Li_2CO_3 have been added. The soln. is heated under a reflux condenser for 1 hr. and then allowed to cool 24 hrs. The least sol. soaps crystallize out and are sepd. by filtration and straining. The alc. soln. is distd. until foaming hinders the operation. Upon cooling, an abundance of pearly white crystals forms; they are sepd. by straining. Two crops of crystals and their mother liquors are treated for the extn. of the fatty acids. The first crystals yield the solid acids; the 2nd crystals yield the liquid acids; the mother liquors give very viscous liquid fatty acids. The acids from the 1st and 2nd crop of crystals are quite sol. in petroleum ether, while those from the mother liquors are only partially sol. The Li soaps of the acid alcs., which are very sol., are found in the mother liquors and this is the first step toward their sepn. From 100 g. of fatty acids, 12.5 g. of solid acids, 62.5 g. of liquid acids and 25 g. of viscous acids are obtained. The solid acids have a mean mol. wt. of 281, I no. 32 and sapon. no. 199; the liquid acids give: mean mol. wt. 287, I no. 131, sapon no. 195; the viscous acids give: mean mol. wt. 277, I no. 110, sapon. no. 202. The mean mol. wt. of the viscous fatty acids is low; this would not seem to corroborate the idea of the presence of ricinoleic acid, whose mol. wt. is 298. E. Scherubel

Palm oil plant. Henri Blin. *Mat. grasses* **13**, 5880–3(1921).—Description of a modern oil plant. E. Scherubel

Comparison of extraction methods for olive oil. H. B. *Mat. grasses.* **13**, 5884–5 (1921).—There are 4 methods for extg. olive oil: chem., diffusion, centrifugal and vacuum. (1) The paste resulting from grinding is mixed with a dil. alk. lye and heated by a steam coil to 40°, while air is injected and an elec. current is passed through. At the end of 6 hrs. the action is stopped and the oil removed and treated with a 1.5% soln. of alum and a certain amt. of sea water. The extn. operation is repeated for 7 to 12 hrs. It is claimed that 26% of oil is recovered by this process as against 23% by pressing; but Bracci states that only 18 to 21% is obtained. The oil is neutral but has a woody taste due to incipient sapon. The cost of the app. and the slowness of the method make it unsatisfactory. (2) The diffusion method is carried out in a battery of vessels used for these operations. Sea water or a soln. of sea salts is used and the mass heated to 30° and agitated with paddles. This method yields 1.6% less than by pressing and the oil is less sweet. The great objection to the process is the cost of installation and the large vol. of H_2O required. (3) By means of a lab. centrifuge operating at a speed of 3000 to 4000 r. p. m. B. obtained in 3 min. 20 to 22% of a liquid contg. 14 to 16% of oil and 6% of H_2O. The addition of hot H_2O and recentrifuging did not yield any more oil. The low yield and poor quality of the oil make the method unsuitable. (4) In the vacuum method the paste is introduced onto a screen in the upper half of a horizontal cylindrical metal drum, the lower part of which is connected to a vacuum pump. The vacuum obtained is equal to a pressure of 1 kg. per sq. cm. while

that obtained by hydraulic pressure is equal to 20 kg. per sq. cm. The first tests in Italy resulted in obtaining 40% of the oil; a 2nd extn. with hot H_2O yielded the balance. None of the 4 methods described gave as good results as the ordinary pressing method. E. SCHERUBEL

The preparation of palm oil for edible purposes. ANON. *Bull. Imp. Inst.* **19**, 64–6(1921).—Bunches of fruits while still on the trees contain loose ripe fruits, and expts. show that these loose ripe fruits give an oil with a considerable acid content. The decompn. of the oil starts at the surface of the loose fruits where they have been joined to the bunch and is accelerated by the presence of moisture and the growth of molds and bacteria. Fruits which have become loosened after gathering the bunch can give an oil with a low acid content if they are immediately sepd. from the bunch and carefully stored in the open air. The decompn. of the oil begins immediately after the cells are broken and the lipolytic enzymes are brought into contact with the oil. The reaction starts rapidly, but after about 40% of the fatty acids have been liberated, it proceeds more or less proportionately to the time. R. L. SIBLEY

Soy-bean oil: Factors which influence its production and composition. C. R. FELLERS. *J. Ind. Eng. Chem.* **13**, 689–91(1921).—Domestic soy-bean oil is identical, chemically and physically, with imported oils. Samples of soy-bean oil from different varieties of beans, subjected to different methods of extn. and lengths of storage, and with different soil conditions and degrees of maturity of the seed when harvested, vary considerably in their physical and chem. properties. The av. amt. of oil from 26 different varieties of beans was 18.3%; Ebony was lowest with 14.8%, while O'Kate was highest with 25.6%. The length of growing season influences the oil content of soy-bean seeds. The oil content becomes less as the date of planting is later in the season. The no. of days required to reach maturity is shortened when plantings are made during the middle and late summer. There is considerable variation in the color and drying power of soy-bean oils derived from the different varieties of beans. When used with suitable driers such as Pb, Co, or Mn tungate or linoleate it may be used alone; otherwise it is expedient to use mixts. up to 50% with tung or linseed oils. E. SCHERUBEL

Barbassu nuts. HENRI JUMELLE. *Mat. grasses* **13**, 5878–9(1921).—The nuts are composed of: H_2O 4.21%, oil 66.12%, carbohydrates 14.47%, albuminoids 7.18%, cellulose 5.99%, ash 2.03%. The oil has the following consts.: m. 26°, solidification p. 22.7°, sapon. no. 247.7, ether no. 242.9, I no. 16.83, R.-M. no. 6.2, Polenske no. 11.3, glycerol 13.2%. The cake has the following compn.: H_2O 11.59, oil 6.50, albuminoids 19.81, carbohydrates 40, cellulose 16.50, ash 5.60%. Over 3-million kg. of these palm nuts, which belong to the genus *Orbignia*, were exported in 1920. The oil is suitable for edible purposes and for soap. E. SCHERUBEL

Method of extracting soy beans by means of a solvent. J. MARTIN. *Mat. grasses* **13**, 5879–80(1921).—The successive steps are as follows: The beans are finely ground and extd. for 30 min. with benzine partially satd. with oil from previous extns. The solvent is then drawn off into a still and more yellow benzine added and allowed to ext. for 40 min. after which the solvent is drained off for 1 hr. Fresh benzine is next added and the residue washed with it for 10 min. This washing is followed by draining for 30 min. when steam is admitted to remove the solvent retained by the cake. This takes about 40 min. and the entire operation of handling one charge takes from 3 to 4 hrs. E. SCHERUBEL

The waste of the soap industry. J. H. CHESTER. *Chem. Met. Eng.* **25**, 445(1921). E. J. C.

Wool oils (MCARTHUR) **25.** Vegetable fats and oils (III) drying oils (RINDL) **11D.** The prickly pear. Possibilities of its utilization (JURITZ) **12.** Apparatus for extracting oils, fats, grease or other materials with solvents (U. S. 1,381,758) **1.**

Purifying fatty glycerides. E. KLEIN. U. S. 1,381,564, June 14. Purified glycerides are obtained from oils such as linseed, cottonseed or maize oils, by heating the oil and treating it with heated compressed air (which has been passed over hot chem. agents such as CaO, Zn dust, S and Cu or their reaction products) and with $NaHSO_3$ and $Na_2S_2O_4$, NaOH sufficient to neutralize acidity, followed by fractional congealation to produce *food products* or material for other purposes, having a desired m. p.

Separating oleo and stearin from fats. C. H. HAPGOOD. U. S. 1,381,705, June 14. In sepg. oleo and stearin from fats, the fat is mixed with a liquid heavier than oleo, *e. g.*, H_2O, and the oleo is centrifugally sepd. from the mixt. The stearin and associated liquid are then centrifugally sepd. from each other.

Separating oils from foots. C. H. HAPGOOD. U. S. 1,381,706, June 14. In treating oil and foots, coarser particles are sepd. out and the partially purified material is then subjected to centrifugal action together with heated H_2O or other liquid heavier than the oil and the oil is thus sepd. from the other liquid and associated impurities, and a portion of the heated liquid, after freeing it from residual suspended particles, is reused for continuing the centrifugal sepn. of oil. The method is especially adapted for treating foots from cottonseed, copra or palm nuts.

Hydrogenating oils. A. J. MCDOUGALL. U. S. 1,381,319, June 14. The pat. relates to mechanical features of circulating oil, catalyst and H together.

Treating catalysts from oil hydrogenation. W. HOSKINS. U. S. 1,381,558, June 14. Catalysts such as Ni and a carrier from oil hydrogenation are mixed with dil. H_2SO_4 or other suitable solvent acid and heated to a temp. of about 52–82° in order to liquefy the fat present and the mixt. is then filtered to sep. out the carrier.

Nickel catalyst for hydrogenating oils. C. B. CLUFF. U. S. 1,381,969, June 21. The catalyst is formed by subjecting a mixt. of Ni carbonate, Ni formate or similar reducible Ni compd. with melted tallow to the reducing action of H at a temp. of about 240–5°.

Soap manufacture. JOEL STARRELS. Can. 212,284, June 28, 1921. An unsatd. solid or semisolid fat, such as tallow or grease, is subjected to the action of H in the presence of finely divided Ni to sat. the fat with H, thus reducing its I number to zero and raising its m. p. to 62°; hydrocarbons and coloring matters are formed. The fatty glyceride is subjected to a splitting process to sep. the glycerol from the fatty acids. The coloring matters are removed and a pure fatty acid of high m. p. and good color is obtained.

28—SUGAR, STARCH AND GUMS

F. W. ZERBAN

New method for the volumetric determination of reducing sugars. AL. IONESCU AND V. VARGOLICI. *Ann. chim. anal. chim. appl.* 3, 229–34(1921).—See *C. A.* 14, 3812. E. J. C.

Improvements to be realized in the cane sugar industry. C. E. COATES. *Chem. Met. Eng.* 25, 438(1921). E. J. C.

The cultivation of sugar cane and the manufacture of cane sugar. ANON. *Bull. Imp. Inst.* 19, 26–59(1921).—This article is a general account of the cultivation of sugar cane and of the manuf. of cane sugar. Statistics and production figures of the various countries are given. R. L. SIBLEY

Composition of sugar beets destroyed by Rhizoctonia. VLAD ŠKOLA. *Z. Zuckerind. Böhmen* 42, 135–8(1918); *Botan. Abstracts* 5, 274.—Affected tissue contains invert sugar but no sucrose. H. G.

High-polarizing beets and their progeny. J. URBAN. *Z. Zuckerind. Böhmen* 42, 387–91(1919); *Botan. Abstracts* 6, 164.—Three groups of mother beets whose av.

sugar contents were 20.28, 20.66, and 21.14%, resp., gave progeny whose averages were 21.47, 21.29, and 21.59% sugar. Three generations showed no noticeable influence of small differences in sugar percentage of mother beets upon averages of progeny. Same mother beets seriated for wts. showed a negative correlation between size and sugar percentage. H. G.

Studies on starch. A. REYCHLER. *Bull. soc. chim. Belg.* **29**, 309–17(1920).—The gelatinization of starch can be conveniently followed microscopically at ordinary temps. by using a soln. contg. about 0.135 mol. of alkali hydroxide per l. A similar action is produced by 4 *N* or 5 *N* acids and by certain concd. salt solns., such as 30% NH_4NO_3, 15% KCNS, etc. The reverse action is produced if to 100 cc. of a starch paste, 80 g. of Na sulfate, 40 g. of NH_4 or Mg sulfate, etc., are added, a complete coagulation resulting in a few mins. regardless of the temp. Under ordinary conditions this retrogradation takes 10 or 12 days, and is then only partial. The microscopical observations may be interpreted by postulating that the starch mucilage is a suspension of swollen and partially burst granules consisting of an internal substance and an envelope which is impenetrable by water unless at an elevated temp. or in presence of an alkali, etc., when it becomes hydrated and allows the internal material to form a voluminous gel or sol. The coagulum produced by Na sulfate, etc., is composed of amorphous granules, smaller in size than the swollen granules of the mucilage, and formed by the shrinking of the envelope and the consequent expulsion and coagulation of the internal sol. Starch solns. formed by heating the mucilage at 120–150° exhibit a similar phenomenon of coagulation, and the ppt. formed can readily be isolated by taking advantage of its resistance to diastase. On drying it forms a hard, warty mass, resistant to all reagents except potash, but still showing under the microscope its constituent globules. It is dissolved by water at 150°, and the solns. resemble those of the original starch, but are characterized by giving a deeper blue color with I, and by yielding an almost theoretical quantity of maltose when treated with malt ext. It appears, therefore, to be composed exclusively of a polysaccharide (amylose), while the original starch contains in addition a more refractory substance originally designated by Maquenne amylopectin (cf. *C. A.* **1**, 246). Amylose can therefore be characterized as a solid, relatively sol., in the starch granules; colloidally dissolved and coagulable in the internal fluid of the granules in the mucilage, in starch solns., and in solns. of the coagulum; solid and attackable with difficulty in the coagulum. Amylopectin is met with as a solid, dense and resistant in the envelope of the starch granules; as solid, but swollen, permeable by water and liquefiable by malt ext., in the granular envelopes of the mucilage; and also dissolved in the starch solns. J. S. C. I.

Report of the Imperial Agricultural Chemist (HARRISON) **15.** The polyoses of rotted beets (VOTOCEK) **10.**

Sugar purification. J. J. HOOD. Can. 212,596, July 26, 1921. Colored contituents are removed from saccharine materials by filtering the materials through ignited and pptd. Al_2O_3 or bauxite. Cf. *C. A.* **14**, 863.

29—LEATHER AND GLUE

ALLEN ROGERS

The leather trade as a chemical industry. A. HARVEY. *Chem. Age* (London) **5**, 238(1921). E. J. C.

Inefficiency in the leather industry. JOHN ARTHUR WILSON. *Chem. Met. Eng.* **25**, 436(1921). E. J. C.

Gambier and its adulteration. J. TEMMINCK GROLL. *Ber. Afdeeling hand. Ko-*

Ioniaal Inst. **1920**, No. 3, 12 pp.—Gambier is an ext. obtained in the Dutch East Indies by boiling the leaves and twigs of *Uncaria gambier Roxb.* It is also known as *catechu, yellow cachou, cutch* and *cutah.* The results are given of the examn. as to soly. in 90% alc., ash content, behavior in water, Dieterich reaction, and appearance, of 24 samples of various gambiers. NATHAN VAN PATTEN

Preparation of leather scrap for the manufacture of glue. ANON. *Farben-Ztg.* **26**, 1977(1921).—Tanned leather must be pulverized and heated under pressure with $Ca(OH)_2$ or NaOH to remove all tannic acid. Boiling the scrap with oxalic acid and then mixing with slaked CaO, exposing the mixt. to the air for several wks., and finally washing out the Ca with dil. HCl is sometimes resorted to. This treatment is not adaptable to chrome tanned leather, which must be treated for a long time with 40% H_2SO_4, then washed in order with H_2O, milk of lime, dil. HCl, dil. NaOH, and finally with H_2O until free from alkali. F. A. WERTZ

Outstanding causes of waste in the glue industry. R. H. BOGUE. *Chem. Met. Eng.* **25**, 443–4(1921). E. J. C.

Efforts to eliminate wastes in the glue industry. T. R. TENNANT. *Chem. Met. Eng.* **25**, 443(1921). E. J. C.

Iron salt (U. S. pat. 1,383,264) **18.** Dyeing animal fiber (U. S. pat. 1,383,092) **25.**

Leather substitute. D. BEATTY. U. S. 1,382,947, June 28. A leather substitute is formed of coagulated pliable and moisture-resistant viscose contg. cow hair or other fibrous material.

Leather dressing. C. A. BUMPASS. U. S. 1,382,468. June 21. A dressing for shoes or other leather goods is formed of tallow 10 lbs., neat's-foot oil 5 lbs., beeswax 1 lb., pine tar 1 pint, glycerol $^1/_2$ pint, paraffin 8 oz., and coloring matter.

Deliming hides. W. SAVAGE. U. S. 1,382,124, June 21. Depilated hides are delimed by subjecting them to the action of a paste contg. fullers' earth and H_2O with or without subsequent use of lactic acid.

30—RUBBER AND ALLIED SUBSTANCES

JOHN B. TUTTLE

Rubber in 1920. Annual report of advances in rubber chemistry. EWALD FONROBERT. *Kolloid-Z.* **29**, 148–56, 200–4(1921); cf. *C. A.* **15**, 959.—A review with bibliography. E. J. C.

The use of rubber in the manufacture of rubber goods. BAUMANN. Frankfort. *Z. angew. Chem.* **34**, Aufsatzteil, 375–6(1921).—A superficial presentation of the importance of the rubber industry. It includes the sources, production, markets, compounding, curing and testing of rubber. C. C. DAVIS

Examination of a sample of so-called semi-synthetic rubber. P. NICOLARDOT. *Ann. chim. anal. chim. appl.* **3**, 176–9(1921).—Properties and analysis of an unknown rubber-like material are reported to show the methods of attack necessary in such instances. The color was brown-black by reflected, violet-red by transmitted light. It was elastic, easily compressible, of low tensile strength, and had a sweet taste. It was sol. in boiling H_2O, with a small residue in suspension. There was no $C_3H_5(OH)_3$ present. It burned with an odor of toasted bread, leaving a bulky coke. Analysis gave 13.76% H_2O, 2.85% insol. in H_2O (probably impurities), 6.13% N and 1.32% ash. The residue in boiling H_2O was cellular fiber and sand. The sample softened at 90°, formed 2 layers at 125° and at 132° swelled. Microscopic examination of the residue after heating with concd. HNO_3 and H_2SO_4 showed the presence of 2 diatoms:

(1) *pseudo-navicula* in the largest quantity and (2) *pseudo-asterionella*. There was no *arachnoidiscus-japonicus*, the diatom present in the commonest gelatin. It is judged from these data that the material is made by milling or molding to a dough while hot certain unusual vegetable gelatins found in Japan and the Baltic Sea. C. C. DAVIS

The presence of manganese in raw rubber and the origin of tackiness. G. BRUNI AND C. PELIZZOLA. *India-Rubber J.* 62, 101–2(1921).—The Mn content of tacky samples of *Hevea* rubber is found to be much greater than that of sound samples. In 11 sound samples it averaged 0.16 mg. per 100 g. (range: 0.0625 to 0.250 mg.). In 6 severely tacky samples it was about 100 times as much, and in 6 lightly tacky samples not less than 8 times as much as in the sound samples. G. S. WHITBY

Aging of plantation rubber. H. P. STEVENS. *Bull. Rubber Growers' Assoc.* 3, 289–91(1921); cf. *C. A.* 15, 3001.—7 samples of plantation rubber, of various origins, and ranging in age from 3 to 13 years, gave satisfactory figures in vulcanization tests, with the exception of a low figure for breaking stress shown by one of the samples. G. S. W.

Ten years' experience with aging tests. WILLIAM C. GEER AND WALTER W. EVANS. Akron. *India Rubber World* 64, 887–92(1921).—The history of earlier attempts to devize a satisfactory accelerated life test is outlined, with particular reference to the scheme developed at the B. F. Goodrich Co. (*India Rubber World* 55, 127 (1916)). Typical time-deterioration curves for elongation and tensile strength are discussed for several rubber compds. There is found a correlation between natural and accelerated deterioration. No attempt is made to explain the chem. reactions involved in deterioration, but the hypothetical assumption is made that formation of unstable peroxides and increase in the coeff. of vulcanization take place. It is concluded in general that: (1) it is more reliable to compare rubber compds. graphically than by calcd. % deterioration; (2) rubber compds. in an accelerated life test are not hardened as in natural aging, but become progressively weaker; (3) S changes are not of significance, but can be detected; (4) the method is unreliable for compds. with original tensile strength below 1000 lbs. per sq. in.; (5) the time ratio of the accelerated and natural life tests was so chosen that the accelerated life test is more severe than natural aging; (6) in most cases premature deterioration is due to a wrong cure, chiefly overcure, and the life test is most useful for detg. correct cures; (7) it is a limited comparative method only and is not practicable for comparing compds. of different types, and (8) 1 day of accelerated aging is equiv. in deterioration to approx. 6 mo. of natural aging. C. C. DAVIS

Air conditioning in rubber manufacture. J. ESTEN BOLLING. Newark. *Rubber Age* 9, 375–8(1921).—A popular presentation of humidifiers based on the ejector system, the physics involved, and their application to the rubber industry. Cf. *C. A.* 14, 442. C. C. DAVIS

The detection of accelerators. D. F. TWISS AND G. MARTIN. *Rubber Age* 9, 379–80(1921); *India Rubber J.* 61, 1283–4(1921).—The detection of org. accelerators by total N detn. is useless. They can, however, be nearly all extd. with Me_2CO, whereas the N of most other ingredients remains behind. Two g. of rubber are extd. several hrs. with Me_2CO (if aldehyde-ammonia is possible, a little HCl is added), the Me_2CO evapd., and N in the residue detd. by the Kjeldahl method. If the N exceeds 0.05%, an org. accelerator is probably present. The identification is often impracticable on account of its decompn. during and after curing. Likewise the % originally present is very uncertain. A tentative scheme useful in some cases is outlined, covering aldehyde-ammonia (A), nitroso compds. in general (B), $Me_2NC_6H_4NO$ (C), hexamethylenetetramine (D), furfuramide (E), hydrobenzamide (F), alkylamines (G), and alkylammonium dithiocarbamates (H). B imparts a characteristic color to the Me_2CO

ext., and its Me_2CO or HCl ext., treated with H_2S and $FeCl_3$ solns., gives a methylene blue coloration. Treated with Zn and HCl, cooled, $NaNO_2$ added, poured into β-naphthol with excess of NaOH, it gives a red ppt. The HCl ext. changes its color when made alk., and this color can be extd. with Et_2O. A positive test of a H_2O ext. with Nessler's soln. indicates A, C, D, E, F, G or H. If the distillate from a HCl ext., made alk., shows an NH_3 test, B, E, F, G, H or urea derivs. may be present. A "mustard oil" odor in the HCl ext. indicates a thiocarbanilide. If the HCl ext., diazotized as above, gives a red ppt., it indicates $PhNH_2$, $MeC_6H_4NH_2$, p-$C_6H_4(NH_2)_2$, derivs. of aromatic amines with aldehydes ($PhNCH_2$, PhCH:NPh, etc.) or derivs. of aromatic amines with CS_2 or $Ph_2NC(NH)NHPh$. If all tests are negative, the Me_2CO extract in H_2O soln. must be tested for specific alkaloids. The dithiocarbamates are difficult to identify because of their usual very low %. Indirectly they may be suspected by chem. analysis of the rubber, such as a very low S coeff. C. C. DAVIS

Apparatus for extracting rubber or other materials with solvents (U. S. pat. 1,381,758) **1**. Fabric for airships (U. S. pat. 1,381,412) **25**.

Coagulating rubber latex. S. C. DAVIDSON. U. S. 1,381,455, June 14. See Brit. 159,602(*C. A.* **15**, 2213).

Reclaiming rubber. E. MUSCHEWSKE and W. W. WOOD. U. S. 1,381,654, June 14. Old rubber stock is finely divided and molded under high pressure while heated and is then allowed to stand in the air until cool and reheated to about 150° for about 1 hr. under pressure to form tire treads or other articles.

Vulcanized rubber articles. W. C. GEER. U. S. 1,382,774, June 28. Rubber is mixed with a vulcanizing material such as S and after suitable mastication is formed into lumps. The material is then subdivided into small lumps and the latter are pressed into form and vulcanized. This method is suited for the production of solid cushion tires or similar articles.

Devulcanizing rubber. W. B. PRATT. U. S. 1,382,669, June 28. Vulcanized rubber is subjected to the action of oxalic acid soln. at a temp. of about 140° in order to effect devulcanization. The heating may require 24 hrs. and the rubber is then freed from S by use of solvents.